LABORATORY MANUAL
OF
COLLOID CHEMISTRY

BY

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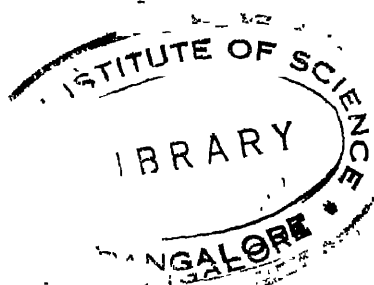
1922

PREFACE

THIS manual was written at the request of the Colloid Committee of the National Research Council.

Most of the experiments have been tested in the laboratory course given at Oberlin for the past six years, while others have been contributed by the leading colloid chemists of this country.

There has long been need of a suitable laboratory manual to advance the teaching of colloid chemistry, and for lack of such a book instruction has lagged. Lecture courses in plenty are given at various universities, but in very few institutions is there a real laboratory course in the subject. It is the laboratory method of instruction that has advanced science so wonderfully in the last half century; obviously, instruction in colloids must develop in the same way.

The general interest in the subject grows apace. Not only theoretical chemists but industrial men as well are expressing the belief that a great many of their problems are colloidal. Hundreds of able chemists would study colloid chemistry in their private laboratories if a self-teaching manual were available. To meet this demand this manual offers a large amount of text material in the way of comment and explanation. The carefully selected references for collateral reading will guide the experimenter and enable him to pursue his studies with a minimum of wasted effort. It is, as the author knows from personal experience, very difficult for the beginner in the subject to know what to read first, or what experiments are worth performing.

Twenty years ago, when colloid chemistry was still in its swaddling clothes, chemists concerned themselves too much with the mere preparation of new colloids, just as organic chemists once prided themselves too much on the mere preparation of new compounds. Now we are making genuine progress by a more intensive study of the properties of material in the colloid state,

by discovering general principles and by the use of quantitative methods.

In preparing this manual the author has been greatly helped by advice and criticism from Mr. Jerome Alexander of the Uniform Adhesive Co., Professor W. D. Bancroft of Cornell University, Dr. Martin H. Fischer of the Cincinnati General Hospital, Dr. Leon Parsons and Mr. Robert E. Wilson of Massachusetts Institute of Technology, Dr. Ellwood Spear of the Goodyear Rubber Co., Dr. S. E. Sheppard of the Eastman Kodak Co., Dr. J. A. Wilson of the Gallun Tanneries at Milwaukee, and Professor J. H. Mathews of the University of Wisconsin.

A number of detailed experiments were generously given by Mr. Alexander (on the ultramicroscope), by Professor Bancroft (on dyeing), by Dr. Spear (on rubber), by Dr. Sheppard (on silver nuclei), by Dr. J. A. Wilson (on tanning) and by Dr. Parsons (on varied topics).

Most of the chapter on Adsorption of Gases was used by permission of the Silica Gel Co. of Baltimore and represents the work of Dr. Patrick. Cuts were loaned by Dr. Martin H. Fischer, the Central Scientific Co. and the Telling-Belle Vernon Co.

HARRY N. HOLMES.

OBERLIN, OHIO, March, 1922.

SELECTIONS FOR SPECIAL COURSES

It is not expected that any one student shall perform all the experiments in this manual. If he did he would probably spend two full days each week for a year in the colloid laboratory.

The teacher must use judgment in selecting representative experiments from each chapter to suit the time allowed for the course. There is a distinct gain in general interest if similar experiments are given to different students rather than to give all exactly the same drill.

Again we must admit that a single definite list of experiments does not meet equally well the needs of students interested in a general fundamental course, in medical work, in agriculture and ceramics, in geology and in industrial work. To meet these different demands the author suggests the following courses based on a time allowance of at least twelve clock-hours per week for one semester:

A General Course.—Experiments 1, 2, 5, 6, 7, 10, 12, 15, 17, 20, 25, 26, 29, 38, 40, 41, 42, 44, 47, 48, 49, 56, 59, 60, 62, 63, 65, 67, 68, 69, 71, 74, 76, 78, 84, 89, 91, 94, 95, 96, 98, 100, 101, 103, 104, 105, 107, 110, 111, 113, 115, 116, 125, 128, 129, 133, 138, 134, 135, 136, 138, 139, 140, 141, 144, 148, 150, 151, 153–159, 160, 161, 165–166, 167–174, 175, 176, 177, 181, 184,

A Course for Medical Students.—Experiments 1, 6, 8, 11, 12, 15, 17, 20, 25, 31, 39, 41, 44, 47, 48, 49, 52, 53, 54, 56, 57, 60, 62, 64, 65, 67, 68, 69, 71, 73, 74, 75, 80, 81, 82, 83, 84, 85, 86, 89, 91, 92, 93, 95, 96, 98, 99, 101, 104, 110, 112, 115, 119, 126, 133, 135, 144, 148, 150, 153–159, 182.

A Course for Students of Agriculture or Ceramics.—Experiments 1, 4, 6, 10, 12, 13, 17, 21, 25, 31, 39, 40, 44, 46, 47, 48, 49, 50, 56, 57, 58, 59, 63, 65, 67, 68, 69, 72, 80, 84, 91, 94, 95, 96, 98, 100, 101, 104, 105, 112, 115, 122, 123, 133, 134, 144, 147, 148, 153–159, 162, 163, 164, 182, 184.

A Course for Students of Geology.—Experiments 1, 3, 4, 10, 12, 13, 17, 21, 25, 31, 40, 43, 44, 46, 47, 48, 49, 50, 56, 57, 58, 59, 63, 65, 67, 68, 69, 71, 72, 84, 91, 95, 100, 106, 115, 122, 123, 125, 127, 128, 133, 134, 144–152, 159–164, 182, 184.

A Course for Students of Industrial Chemistry.—Experiments 1, 2, 3, 10, 12, 13, 16, 21, 25, 31, 41, 42, 46, 47, 48, 50, 55, 56, 57, 58, 59, 65, 67, 68, 69, 7[illegible]2, 79, 81, 84, 85, 86, 90, 91, 94, 95, 96, 102, 104, 105, 108, 109, 112, 115, 116, 125, 127, 133, 134, 135, 136, 137, 138, 139, 140, 141, 144, 148, 153-159, 160, 161, 165, 166, 167–174, 177, 178, 180, 185, 186.

Quantitative experiments for a course in Physical Chemistry are scattered throughout the book and may readily be selected.

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COLLOID LABORATORY MANUAL

CHAPTER I

SUSPENSIONS—COARSE AND FINE

Exp. 1.—With three sieves, of 50-mesh, 100-mesh and 200-mesh, sift any suitable powder, such as quartz flour, clay or starches, into three grades of particles. Suspend about 1 g. of each in test tubes of distilled water and note the time of settling. Make observations on the portions that settle rapidly. In each case a very small fraction is slow to settle.

What has mere size of particle to do with time of settling?

Exp. 2.—Precipitate barium sulfate cold and attempt to filter it. Now precipitate the salt by mixing the proper hot solutions and keeping hot an hour. Will a filter paper retain the precipitate?

The solubility of small particles, slight though it may be, is greater than that of larger particles (greater surface) This solubility is increased by rise in temperature, so the smaller particles dissolve and the dissolved salt deposits on the larger particles which are in contact with their own saturated solution

Exp. 3. Surface and Solubility.—Kenrick (Jour. Phys. Chem., **16**, 515, 1912) outlines a convincing demonstration of the difference between the solubility of small particles and that of larger particles:

Make a normally saturated solution of calcium sulfate by stirring gently, for some hours, 30 g. of coarsely powdered gypsum in 300 cc of distilled water. The finer particles must previously have been rinsed away with water. This saturated solution may well be kept in contact with the crystals. Now grind some gypsum to an impalpable powder in an agate mortar. To one of two beakers containing about 50 cc. of the previously made "normally saturated" gypsum add about 0 5 g of the gypsum powder. Shake a moment and filter twice if not clear With the greater surface more gypsum dissolves, although the solution was saturated with the larger particles

A duplicate of the "normally saturated" solution is filtered at the same time (both portions handled rapidly). To 20 cc. of each filtrate is added 10 cc. of a solution prepared as follows· 100 g. $Na_2HPO_4 \cdot 12H_2O$ and 2.5 g NaOH made up to 1000 cc and 29 cc. (exact amount to be found by titration) of this are colored a deep pink with phenolphthalein and diluted to 100 cc.

The liquid shaken with the finer powder turns colorless, but the other remains pink. An actual titration would show a difference of 10 per cent in

the concentration of calcium sulfate. If the difference in color is not sharp with addition of 10 cc. try 10.5 cc.

Exp. 4.—Problem in analysis: To titrate any unused $Ca(OH)_2$ when carbon dioxide is run into clear limewater. Hydrochloric acid neutralizes unused $Ca(OH)_2$ and then attacks the precipitated $CaCO_3$

First try heating this limewater, with its suspended $CaCO_3$, for fifteen minutes at about 60°. The $CaCO_3$ particles grow in size, probably becoming crystalline and compact, offering far less surface to attack the acid In fact they settle out rapidly. They now dissolve so slowly in dilute acid that the end point with phenolphthalein can be secured before the $CaCO_3$ is attacked noticeably.

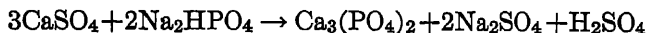
Exp. 5.—Project a powerful beam of light from some source into a small jar or flask containing an As_2S_3 sol (or any colloid at hand) and note whether the path of the beam becomes strongly luminous. Luminosity of the path of the beam is known as the Tyndall effect and indicates the presence of suspended particles, provided that this luminosity is not due to fluorescence.

Insert a Nicol prism between the light source and the colloidal suspension and rotate the prism Note whether there is any change in the intensity of the luminosity as the Nicol is rotated. Such a change in luminosity is to be expected if the luminosity is due to the Tyndall effect, because the light is polarized by reflection from the surfaces of the suspended particles, but it will not be observed if the luminosity is due to fluorescence. (J H. Matthews.)

Compare the Tyndall cone in ordinary water and the same water from which a gelatinous precipitate of $Al(OH)_3$ has settled. Square bottles or small, flat battery jars are suitable for this experiment. What is "optically clear" water?

Exp. 6.—Pour 2 cc of a 10% alcoholic solution of rosin or mastic into 100 cc. of water and get a suspension of minute solid particles of mastic in water. Pour an acetone solution of any liquid fat into water and get a suspension of minute liquid particles of fat in water. It is a general principle that if A is soluble in B but is insoluble in C, A will be thrown into suspension, frequently colloidal, when a solution of A in B is added to an excess of C (if B and C are miscible).

The color change is explained by the reaction:

$$3CaSO_4+2Na_2HPO_4 \rightarrow Ca_3(PO_4)_2+2Na_2SO_4+H_2SO_4$$

The more calcium sulfate there is in solution, the more sulfuric acid is set free to react with the small amount of base present. Of course, the exact amount of base must be carefully adjusted to show the difference expected.

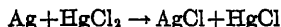
Hulett (Zeit. phys. Chem., **37**, 385, 1901) found that a coarsely crystalline calcium sulfate (1.8μ) was soluble 2.29 mg. per liter at 25°, while the solubility of the same gypsum ground in an

agate mortar to 0.1μ rose to 4.5 mg. per liter. Red mercuric oxide becomes yellow on grinding, and its solubility increases threefold.

Surface increases enormously with subdivision, and all surface phenomena become greatly magnified. A cube, 1 cm. on edge, when subdivided into cubes 10$\mu\mu$ on edge, would possess a total surface of 600 square meters, and the number of particles would be 10^{18}.

Interesting experiments may be devised for the use of the Kober nephelometer in determining the amount of suspended material. Read the excellent discussion of nephelometry by Kober and Graves (Jour. Ind. Eng. Chem., **7**, 843, 1915).

Exp. 7.—Add a saturated solution of mercuric chloride to colloidal silver which the instructor has previously prepared The dark color disappears, and a milkiness, due to the precipitation of white mercurous chloride and silver chloride, appears

$$Ag + HgCl_2 \rightarrow AgCl + HgCl$$

This reaction becomes apparent when silver in colloidal form, with enormous surface, is used although, of course, some reduction must occur when silver foil is used.

THE COLLOID CHEMISTRY OF FEHLING'S TESTS [1]

Exp. 8.—When Fehling's solution is treated with a reducing substance it is generally expected that a bright-red precipitate will be obtained. Frequently, however, an orange or yellow precipitate is obtained, and in certain instances nothing but a yellowish-green discoloration results.

These color changes are coincident with differences in size of particles of the cuprous oxide formed The smallest particles are yellowish green, as they grow in size they become yellow, then orange, and when very coarse they are red When the bright-blue Fehling's solution is mixed with a little dextrose solution, or some diabetic urine, and the mixture is not boiled as ordinarily, but is allowed to stand several hours at room temperature, this series of color changes, beginning with bluish green and ending with red, is observed. Drops of these suspensions examined under the microscope show the corresponding growth in size of particle

Mix cold 1.5 cc of Fehling's solution and 20 cc of 2 per cent dextrose In 30 minutes the colors change from green to yellow to orange and in 7 hours to red.

[1] Adapted from Martin H Fischer, Science, **45**, 505, 1917 See also Journal of Laboratory and Clinical Medicine, **3**, 368, (1918)

In the action of the alkali of Fehling's solution upon dextrose, for example, there are produced, from a chemical point of view, not only the various degradation products which are responsible for the reduction of the copper salt, but from a colloid point of view, certain hydrophilic colloids which tend to inhibit a precipitation of the cuprous oxide in coarse form.

To allow adequate time for the growth of the cuprous oxide particles to the red form, it is better to make reductions at low temperatures than at higher ones.

With much sugar present the number of points at which the copper salt is attacked and reduced will evidently be much larger than when less sugar is added. All the available copper salt for further growth of the particles will, therefore, have been exhausted when the copper oxide particles are still small. Therefore too much reducing sugar is likely to yield only the greenish discoloration. In such cases dilution or reduction and long standing at room temperature may help.

It might be well, before testing for sugar, to boil and filter urine in order to remove any albumin present. Albumin is a protective colloid.

An interesting presentation of **von Weimarn's** law is found in Ostwald's "Theoretical and Applied Colloid Chemistry" and in Washburn's "Principles of Physical Chemistry," 432, 1921, pages 24–33. As demonstrated with Prussian blue and with barium sulfate the size of precipitated particles is greatest when medium concentrations of the two reacting solutions are used. With very low or very high concentrations the precipitated particles are smaller.

Exp. 9.—To 10 cc. of M/200 $FeCl_3$ add 10 cc. of M/200 $K_4Fe(CN)_6$ solution, dilute to about 100 cc. and note whether the solution is clear. Repeat the experiment, using M/10 solutions and explain the difference in the phenomena observed.

Add 5 cc of a practically saturated solution of $FeCl_3$ to 10 cc. of a practically saturated solution of $K_4Fe(CN)_6$ Take a small quantity of the gel and stir up in water. Prove by filtering that the resulting suspension is colloidal.

CHAPTER II

DIALYSIS AND DIFFUSION

GRAHAM distinguished between " colloids " and "crystalloids" by diffusion and dialysis tests. Colloids he classed as substances with a much lower rate of diffusion than crystalloids. Furthermore he observed that some substances diffused through various animal and plant membranes while others did not. Thus with bladder or parchment separating pure water from water containing both colloids and crystalloids he was able to dialyze or purify the colloid suspension, in other words, free it from the so-called crystalloids. For such a process, dialysis, we now use gold-beater's skins (the peritoneal membranes of cattle), collodion membranes, parchment paper and fish bladder. For ultrafiltration read page 115.

Exp. 10.—With a narrow flame or a hot wire cut off the bottom from wide-mouthed bottles. Tie membranes (parchment paper, bladder, gold-beater's skin, collodion, etc) tightly over the mouth, invert the bottle, add liquid; if no drops form on the lower side, the dialyzer is free from leaks. Use 2-inch dialyzing tubes made by Central Scientific Co., Chicago, and Scientific Materials Co , Pittsburgh, or flanged test tubes open at both ends, or make parchment-paper cups of any size, as described by Holmes, Jour. Am. Chem. Soc., **38,** 1203 (1916).

A quotation from this reference follows:

" The cheapest and most easily made dialyzer I have used is a sheet of parchment paper shaped like a beaker. In other words, it is all membrane and has a much greater dialyzing surface than the usual forms. These beakers or cups can be shaped easily by any student. A sheet of parchment, free from pin-holes, is soaked in water a few minutes to soften it and then folded over a bottle of the desired size and shape. The folds should be triangular and narrow, and should cover each other much as do the folds of an umbrella. It is best to crease them moderately. A cord is tied around the paper and bottle about 1 centimeter from the upper edge, and the whole set aside to dry. When dry, the bottle is

removed, and the cup holds its shape perfectly. The cord must be left on the cup to support the sides. Two holes may be punched near the top of the paper and a string attached like the handle of a pail. So tough is the paper that a parchment cup holding a liter of water may be carried without tearing or collapsing. Trimming the upper edges of the cup gives a neater appearance. Three cords may be attached by wire clips as an improvement on the pail.

"When such a dialyzer is to be used it is nearly filled with the colloidal solution and suspended in a large vessel of pure water. Removal of ions is extremely rapid, in spite of the fact that parchment is inferior as a membrane to gold-beater's skin. It is evident that with a given membrane the rate of dialysis is proportional to the effective surface of the membrane. In this form the bottom and sides of the cup are all effective.

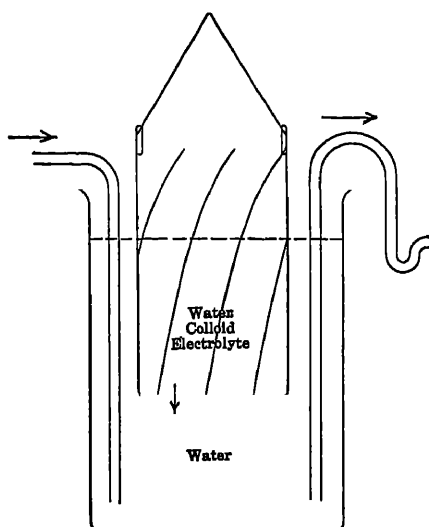



FIG. 1 —Parchment dialyzing cup

"The rate of dialysis may be doubled if two such cups are used, the smaller inside the larger. The inner cup holds pure water and the other the colloidal solution, while the combination of cups is hung in a larger vessel of pure water. This arrangement gives dialyzing surface outside and inside the colloidal solution. The water may be changed as desired."

In dialysis it must be remembered that the non-colloids will diffuse back through the semi-permeable membrane unless the outside water is changed frequently or continuously. A constant level siphon, as shown in Fig. 1, is useful. For many purposes a few days' dialysis may serve; but for very accurate work dialysis must be continued for a few weeks. Hot dialysis, by increasing the speed of diffusion, hastens removal of impurities.

It is a good plan to soak parchment paper in three or more changes of distilled water before use. In this way the sulfates left from the manufacture of the paper (treatment with sulfuric acid) are removed. Some colloids are easily precipitated by sulfates.

Exp. 11.—To make collodion dialyzers, dip a dry test tube into a solution of collodion in a mixture of dry ether and absolute alcohol, drain for two minutes, and dry by revolving in air When it no longer sticks to the finger on a light touch, immerse in warm water a few minutes. Carefully peel it off Keep it in water. Or *fill* a dry tube or an Erlenmeyer flask, invert, and clamp to drain for a few minutes. When no ether is noticeable, fill with warm water and carefully loosen membrane. By using beakers, larger cups may be made. Permeability depends on the extent of drying before water is added to loosen the film.

Make your own collodion solution. Dry the pyroxylin, dissolve 3 or 4 g. in 100 cc. (25 cc. alcohol+75 cc ether) by first soaking for fifteen minutes in the alcohol and then adding the ether. Stir.

Flat films[1] are made on a glass plate or on mercury

J. M Looney (Jour. Biol Chem. **50**, 1, 1922) outlines a method of preparing very flexible collodion membranes The usual membranes of this type become brittle and stiff if allowed to dry completely so they are kept wet Looney prepared collodion membranes that were very flexible after drying for two weeks and still retained their permeability

Place 5 g. of "Anthony's Negative Cotton," which has been dried 48 hours over concentrated sulfuric acid, in a very clean and dry Erlenmeyer flask Add 25 cc of absolute ethyl alcohol and agitate so that all the cotton is moistened. Now add 75 cc of ether which has been distilled over sodium, and shake until the cotton has completely dissolved Next add 15 cc of dry ethyl acetate with shaking to secure complete mixing of the solvents Let the solution stand overnight and then decant the clean supernatant liquid into another flask

Pour this solution into a large test tube or Erlenmeyer flask (clean and dry) and drain back into the container by holding the flask at an angle of 60° and rotating to secure uniform thickness of film When the liquid no longer drips freely, clamp the flask vertically and let stand until perfectly dry. Then peel off the top of the film from the neck of the flask and loosen by pouring a gentle stream of water between the membrane and the side of the flask Carefully pull out the membrane and test for pin holes by filling with a solution of Congo red and hanging in pure water Permeability may be tested by noting the readiness with which a solution of potassium ferrocyanide diffuses through into pure water

R. E. Wilson and Leon W Parsons modify the method of Wm Brown (Jour.

[1] An egg membrane can be secured by dissolving off the shell in dilute acid. Viscose bottle caps, holding about 100 cc, can be secured from Antoine Chiris Co, 20 Platt St, New York City. They are good dialyzers

Biol. Chem. 9, 320, 1915) in order to prepare suitable large sheets of collodion membrane. A 4 per cent solution of collodion in a mixture of three parts ether to one part absolute alcohol is poured onto a clean, level, glass plate, covering this over with a frame immediately to restrict evaporation of the solvent When the film is dry enough to strip it is cut away with a knife and carefully removed. It is immersed at once in 80 per cent alcohol. After soaking in this for twenty-four hours it is removed and washed for a day in several changes of pure cold water Such a membrane is very permanent in acid or neutral solution but dissolves in alkali.

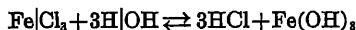
These membranes may be made in bag form by sewing the edges and then painting them with collodion solution.

Bartel and Carpenter will soon publish a paper on "Anomalous Osmose with Collodion Membranes" in which variations in the permeability of such membranes will be discussed.

Get Ansco's "negative cotton" from Ansco Co., Binghamton, N. Y., or "Parlodion" from Du Pont, Wilmington, Del.

Read Bigelow and Gemberling, Jour. Am. Chem. Soc., **29,** 1576 (1907); Walpole, in Biochem. Jour., **9,** 284 (1915); Brown, in Biochem. Jour., **9,** 320, 591 (1915); Farmer, Jour. Biol. Chem. **32,** 447 (1917); Schoep, Koll.-Zeit., **8,** 80 (1911).

Exp. 12.—Make colloidal $Fe(OH)_3$ by pouring a concentrated solution of $FeCl_3$ into a beaker containing 300 cc. boiling water. A rich red solution, which is very stable, is formed instantly.

$$Fe|Cl_3 + 3H|OH \rightleftarrows 3HCl + Fe(OH)_3$$

When it is cold, dialyze portions in different dialyzers, noting the time of appearance of chloride ions in the dialysates. ($AgNO_3$ test.)

Dialyze 200 cc. with frequent changes of water until nearly free from chloride ions. Preserve for "Coagulation" chapter.

A convenient support for large dialyzing tubes may be made by cutting a hole in a sheet of heavy cardboard so that the tube may be held tightly in the hole. With the cardboard on the top of a beaker the tube may be adjusted so that the membrane does not rest on the bottom of the beaker Still better, a circle having the same diameter as the tube may be outlined and five or six radial cuts made with a knife. The triangular projections of cardboard, when bent out and reinforced with a rubber band, help to hold the dialyzing tube.

Exp. 13.—Try to dialyze (small tubes) solutions of blue Congo-red acid (acidified dye), night blue, safranine, fluorescein, sugar, copper sulfate, coffee and other substances Which have colloidal properties?

Exp. 14.—Dialyze a solution of castile soap (about 0.5 per cent) against a relatively small amount of water. Do not change the dialysate After a few days shake some of the dialysate in a test tube. Does it froth like soap solutions? Was any appreciable amount of the soap in true solution at room temperature?

Exp. 15.—Dialyze thin starch paste. Test the dialysate for starch and glucose. Now add diastase (or Fairchild's "Diazyme") to the starch and keep on testing samples of the dialysate for glucose, using Fehling's solution.

Exp. 16.—Dialyzers for Non-aqueous Sols.—Wo Ostwald in a report before the Faraday Society and the Physical Society of London (1920) described a useful method of non-aqueous dialysis Prepare Lottermoser's colloidal mercuric sulfide by passing a brisk stream of washed and dried H_2S for 10 minutes into an alcoholic solution of $Hg(CN)_2$ of any concentration. The alcohol, however, must be 97 per cent, not stronger A deep-brown sol forms. It may be diluted with more 97 per cent alchool and stabilized with more H_2S. In a closed bottle this keeps for weeks.

Compare the dialysis of this colloid (an alcosol) with that of night blue dissolved in 97 per cent alcohol Alcohol must be used on both sides of the membrane Night blue is a colloid in water but is molecularly dispersed in 97 per cent alcohol. Membranes suitable for alcohol dialysis are parchment, collodion, and gelatin hardened with alcohol. Soak paper thimbles in 97 per cent alcohol and then pour into the thimbles ordinary 4 per cent pharmaceutical collodion Drain and dry quickly in warm air until dry to the touch and until the smell of ether is gone. Pour in collodion solution again, drain and dry The membrane is now ready. During dialysis the alcosols must be kept covered to prevent evaporation and the levels of the liquid outside and in the thimble must be kept the same.

"So far," writes Ostwald, "we have not found any substance, spontaneously soluble in 97 per cent alcohol, which would not dialyze or diffuse to a perceptible degree Even resins such as copal, mastic, dammar and dragon's blood dialyzed in 97 per cent alcohol, as did alcoholic linseed oil, beeswax, lard, aluminum oleate, etc" Even the zein of corn diffused

Permeability is tested by dropping the dialysate into a beaker of water or a solution of alum After 24 hours some milkiness is always observed Any collodion precipitated appears in films or scales, not as a milky suspension.

HOT DIALYSIS [1]

The speed of dialysis depends upon the following factors: First, the nature of the membrane; second, the area of the membrane which is in contact with liquid on both sides; third, the difference in concentration of diffusible substances in internal and external liquids close to the membrane; fourth, the temperatures of the internal and external liquids.

Hot dialysis, with its greater speed of diffusion, enables us to hasten greatly the purification of colloids. A parchment paper sack, A (prepared wet), of about 1 liter capacity, is nearly filled

[1] Method of Marks Neidle, Jour. Am. Chem. Soc, **38**, 1270 (1916); **39**, 71 (1917).

with distilled water and then suspended in a 2-liter beaker containing 500–1000 cc. of the solution to be dialyzed. Distilled water is run through the sack at a rate of about 2 liters per hour, the level being kept constant by means of an automatic siphon. The folded neck of the paper sack is tied to the flanged end of a glass tube (15 cm. long and 2 cm. in diameter). The colloidal solution in the beaker is heated, usually to 70°–90°,

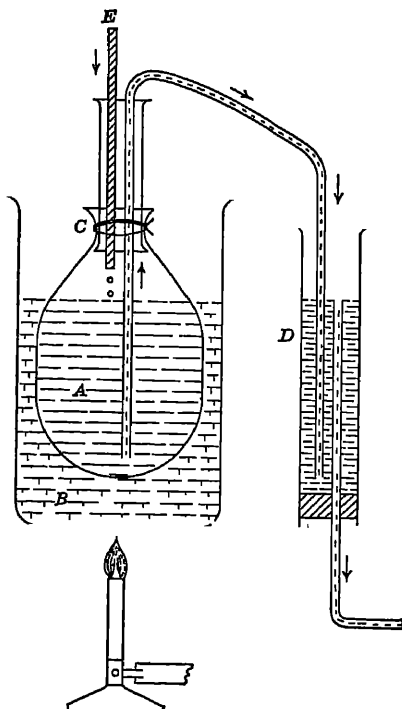



FIG. 2.—Hot dialysis.

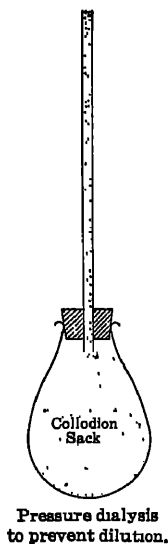



FIG 3.

By placing the colloidal solution to be dialyzed in the outer vessel, the large increase in volume, due to osmosis, is avoided. Evaporation balances the effect of osmotic flow.

A colloidal solution of high purity may be obtained by this method in eight to ten days, while the usual method may require a month. For most experiments even this time of dialysis is excessive.

Exp. 17. Chromium Hydroxide Purified by Hot Dialysis.—Add 49 cc. of N ammonium hydroxide to 162 cc of N chromium chloride with vigorous shaking. This amount of ammonium hydroxide is equivalent to less than half of the chromium chloride, so the hydroxide precipitated at first is peptized (subdivided) by the action of the remaining chromium chloride.

Let stand twenty minutes, or until the precipitate disappears. The resulting clear green solution is diluted to 400 cc. and dialyzed for thirty-four hours at 75°–80° That a nearly pure chromium hydroxide is secured is shown by analysis. The ratio of chromium to chlorine has been found by Neidle to be 65 : 1. If the dialysis is carried on near the boiling point, the colloid secured in ten hours will be as pure as that resulting from seventy-three days' cold dialysis

The volumes given above represent an actual experiment by Neidle and may be varied somewhat.

DIFFUSION

Exp. 18.—Let solutions of Congo red, beet juice, colloidal $Fe(OH)_3$, night blue, coffee, safranine and fluorescein, as well as colored salts, diffuse into jellies of 3 per cent gelatin or 2 per cent agar. Use test tubes more than half full of jelly Which are colloids, as shown by speed of diffusion? Jellies are thick membranes.

Exp. 19. Alexander's "Patriotic Tube."—Fill a test tube two-thirds full with slightly alkaline solution of agar containing enough phenolphthalein to turn it pink, and a little $K_4Fe(CN)_4$. After the agar has set to a solid, a dilute solution of $FeCl_3$ is carefully poured on top The ion forms, with the ferrocyanide, a slowly advancing band of blue, before which the more rapidly diffusing HCl spreads a white band as it discharges the pink of the indicator In a few days the tube is about equally banded in red, white and blue.

The agar may be alkaline as purchased Acetic acid may be added until the pink color of the phenolphthalein is just discharged. Then the color may be brought back with a trace of alkali.

CHAPTER III

CONDENSATION METHODS OF PREPARATION

REACTION between dissolved substances may yield precipitates or may yield those aggregates of a few hundred or thousand molecules that we term colloidal. In the latter case colloidal suspensions are formed by condensation of smaller particles into larger ones.

In the following work distilled water must be used. Since on long storage it may take up impurities from the container or from the air, there are times when freshly distilled water may be necessary. Resistance glass vessels must be used for all work. Inferior results are obtained with the vessels of more soluble glass.

Small Erlenmeyer flasks are useful. The utmost cleanliness must be observed. Glass is best cleaned with warm chromic-acid solution, rinsed with tap water and finally with distilled water. If necessary, the glass should be steamed out.

Dialyzing membranes are used the second time only for purification of the same colloid, and only if they have been kept wet.

REDUCTION

Exp. 20. Preparation of Gold Hydrosol. (Zsigmondy's Method).—The water used for solutions should be distilled twice through a block tin coil condenser. The best American resistance glass, thoroughly cleaned, should be used for all containers.

Three solutions are necessary: (1) 6 g. $AuCl_3 \cdot HCl \cdot 3H_2O$ dissolved and made up to 1 liter with conductivity water, (2) one liter of 0.18 N K_2CO_3; and (3) a 0.3 per cent solution of formaldehyde.

According to Zsigmondy, 120 cc of water prepared as above are heated, and 2.5 cc. of gold chloride solution added, then 3 5 cc. K_2CO_3 solution. This is stirred to insure uniformity and heated to 100° C. It is removed from the heater, and 3 to 5 cc. of the formaldehyde solution are added with lively stirring.

S. E Sheppard and F. A Elliott find a much smaller amount of formaldehyde quite sufficient. They added formaldehyde solution (0.3 per cent, made by adding 0.3 cc. of ordinary formalin to 100 cc. of water) a drop at a time,

stirring well, until a faint red tint appeared. Additions were made only after a color change was no longer produced by the previous drop. A deep red and extremely clear solution was thus obtained. About 2 cc. of the formaldehyde solution were used. Sometimes 4 cc. yields a brighter colloid.

The section on colloidal gold, beginning on page 89 of Zsigmondy's "Chemistry of Colloids" is well worth reading at this point.

Zsigmondy's gold is the form best suited to coagulation experiments and is even used in the study of spinal fluid as an aid to diagnosis.

Exp. 21. Gold by Tannin.—Wo. Ostwald reduces gold chloride with tannin, under conditions that guarantee the finely divided red gold

To 100 cc. of distilled water add a few drops of a 0 1 per cent solution of gold chloride which has been neutralized with the calculated amount of potassium carbonate Now add a few drops of a 0.1 per cent solution of tannin. Heat the colorless mixture a minute or two, shaking it constantly. Below 100° a cherry-red color appears Now add more gold chloride and tannin alternately until the color deepens to suit your fancy.

Tannin has some protective qualities and therefore this method is surer than some others.

One drop of chloroform to 12 cc. of such a tannin preparation kept it free from mold for four months. Tannin solutions have a great tendency to develop mold.

Exp. 22. Gold by Pyrocatechin.—Make a series such as:

Add 0.20 cc of 0 1 per cent pyrocatechin to 10 cc. of 0.1 per cent gold chloride.
Add 2 00 cc of 0.1 per cent pyrocatechin to 10 cc. of 0.1 per cent gold chloride.
Add 5.00 cc. of 0.1 per cent pyrocatechin to 10 cc. of 0.1 per cent gold chloride.

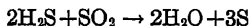
Unstable green gold sols may be secured

Exp. 23. Kohlschütter's Silver.—Kohlschütter reduced silver oxide in water at 50°–60°, with a stream of hydrogen. Thus a sol free from electrolytes was obtained

Make a 5 per cent solution of silver nitrate. Precipitate silver oxide with a slight excess of dilute sodium hydroxide (not ammonia), and wash a few times by hot-water decantation. Make a saturated solution in hot water, filtering off undissolved oxide. Pass a stream of washed hydrogen through the solution of silver oxide (and hydroxide) at 50°–60° for forty minutes The color of the reduced silver depends, curiously enough, upon the nature of the walls of the reduction flask With resistance glass it may be red, violet or blue. Zsigmondy's "Chemistry of Colloids" gives an interesting page (p. 117) to this method.

Exp. 24. Silver by Tannin.—To 5 cc. of 1 per cent silver nitrate solution add very dilute ammonia drop by drop until the precipitate just disappears. Dilute to 100 cc. Mix with 0.4 cc. or more tannin (0.5 g in 100 cc water). Try mixing both hot and cold solutions. Vary the proportions. The colloid is red-brown by transmitted light and olive green by reflected light

Exp. 25. Sulfur.—Pass hydrogen sulfide (washed) into sulfur dioxide water until all odor of sulfur dioxide is gone. (Do not do this in the colloid laboratory.)

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

Precipitate this colloidal sulfur by addition of powdered sodium chloride, shaking. Filter Wash on the filter until all sodium chloride is removed. The sulfur begins to run through the filter in a good suspension Acidified "hypo" yields colloidal sulfur, as do most oxidizing agents on hydrogen sulfide water. The author found gleaming crystals of sulfur in an old suspension of colloidal sulfur. This would seem to indicate a slight solubility of sulfur to make possible the change from the colloid to the crystalloid state.

HYDROXIDES AND OXIDES

(Although for convenience we write $Fe(OH)_3$, it is probable that we deal with different degrees of hydration of Fe_2O_3.)

Exp. 26. Ferric Hydroxide.—The addition of a few cc of concentrated $FeCl_3$ to much boiling water has already been given as one method of preparing ferric hydroxide

We may also boil ferric acetate (made from washed ferrichydroxide and acetic acid) until no more acetic acid passes off, and get the colloid, an example of hot hydrolysis. (Péan de St. Gille's method.)

Read: Jour. Phys. Chem., 232 (1915). Make Krecke's colloid by hydrolysis of 0.1 per cent $FeCl_3$; also by hydrolysis of 0.75 per cent $FeCl_3$ at 87° and 93°; also by hydrolysis of 0.5 per cent $FeCl_3$ at 100°.

These represent different degrees of hydration of Fe_2O_3. The color differences are similar to those in hematite and limonite iron ores.

Exp. 27. Chromium Hydroxide.—To remove the trace of sulfate in most "C. P. chromium chloride," add a little barium chloride to the boiling solution. Dilute greatly and then add ammonia to the boiling-hot chromium chloride to precipitate chromium hydroxide Boil off the excess ammonia (test by odor), let settle, filter and wash the precipitate Dissolve it in boiling 6N hydrochloric acid and evaporate the resulting solution of chromium chloride to a small volume to get the last of the precipitate into solution More hydroxide should then be added Filter, and dialyze. A beautiful, clear, green sol is obtained

Exp. 28. Molybdenum Blue (Mo_3O_8).—Add 5 g ammonium molybdate and 30 cc of 4 N sulfuric acid to 150 cc. of water While it is boiling hot, reduce with a rapid stream of hydrogen sulfide (Hood) Dialyze. Dye a strip of white silk with the blue colloid.

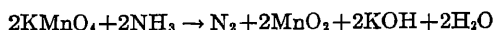
This was reduction in a strongly acid solution (Dumanski's method). Repeat the experiment, using only one drop of sulfuric acid instead of 30 cc. Note the difference in color of the colloid which is probably a different oxide of molybdenum.

Exp. 29. Manganese Dioxide.[1]—" Potassium permanganate is a powerful but relatively slow oxidizing agent . . . and does not react at a measurable rate with ammonium hydroxide at ordinary temperatures. If, however, to a hot concentrated potassium permanganate solution ammonium hydroxide is added, ammonia is oxidized to nitrogen and manganese dioxide is precipitated. If, to a fairly dilute solution of potassium permanganate, concentrated ammonium hydroxide is added slowly, manganese dioxide does not precipitate, but remains in the colloidal form. After trying various concentrations of potassium permanganate and of ammonium hydroxide we obtained the best results by the following method:

" Heat a M/100 permanganate solution to boiling. Then while stirring, add concentrated ammonium hydroxide, one drop every three minutes. At no time should anything but the faintest smell of ammonia be perceptible. The solution should be kept at about 90°. It turns wine-red and finally coffee-brown by transmitted light and a bluish-brown oily color by reflected light. To test if all the permanganate has been reduced, a portion of the colloidal solution can be coagulated by the addition of salt, to show the presence of any violet color which may have been masked by the dioxide.

(About 10 cc ammonia may be added, 1 drop per second)

" As will be seen from the equation

$$2KMnO_4+2NH_3 \rightarrow N_2+2MnO_2+2KOH+2H_2O$$

in the final colloid there is present, beside the dioxide, only some potassium hydroxide, which has a small, if any, coagulating effect. . . Marck has found the colloid is coagulated by contact with filter paper or parchment, so it cannot be dialyzed unless very special precautions are taken. . . . Alcohol does not coagulate the solution "

Colloidal manganese dioxide can also be made by reduction of potassium permanganate with hydrogen peroxide (Marck); by reduction with sodium thiosulfate (Spring and de Boeck); and by reduction with arsenious acid (Deisz). Fremy (Compt. rend., **82**, 1231, 1876) obtained a red solution by treating potassium permanganate with concentrated sulfuric acid (caution!). It is safer to leave Fremy's experiment alone unless the exact directions are at hand. See page 110.

Exp. 30.—Mix 60 cc of 0 3 per cent potassium permanganate with 20 cc of H_2O_2 (commercial 3 per cent plus an equal volume of water) A brown form of colloidal managanese dioxide is secured and is stable for weeks

[1] Eustace J. Cuy, Jour. Phys. Chem , **25,** 415 (1921).

SULFIDES

Exp. 31. Arsenic Trisulfide.—Mix equal volumes of 1 per cent arsenic-trioxide solution (prepared hot and filtered cold) and saturated hydrogen-sulfide water. Or simply pass washed hydrogen sulfide through a solution of arsenious acid. Boil off the excess hydrogen sulfide or remove it cold with a stream of hydrogen.

$$2As(OH)_3 + 3H_2S \rightarrow 6H_2O + As_2S_3$$

Compare with the product obtained by passing H_2S into $AsCl_3$. Why the difference? Write the equation.

Exp. 32. Antimony Trisulfide.—From a dropping funnel drop a 1 per cent tartar emetic solution into water through which washed H_2S is passing. A beautiful, rich orange-red sol forms. Dialyze. It may remain in suspension several weeks.

Exp. 33. Mercuric Sulfide.—Mix 200 cc. of M/8 mercuric cyanide solution and 200 cc. of saturated hydrogen sulfide water.

Note that mercuric cyanide is but slightly ionized and therefore there are almost no Hg ions to coagulate the negative colloid. All sulfides in water are negatively charged and hence easily discharged by positive ions, especially by those of higher valance

As stated in the previous experiment, the negatively charged sulfides are best prepared in the colloidal form if polyvalent positive ions are absent, or present in a very low concentration. To form copper sulfide we need some copper ions, but our needs are safely met if a poorly ionized copper complex is formed. Then, as fast as the few copper ions present react with sulfide ions, equilibrium is disturbed and more copper ions form. The tartrates and citrates, or even ammonia, " tie up " copper ions to suit our needs.

Exp. 34. Copper Sulfide.—To 100 cc. of water add 4 cc. of 1 per cent "blue vitriol" and enough dilute ammonia to form the azure-blue soluble complex. Then add 4 cc. of dilute Rochelle salts solution. Pass washed hydrogen sulfide into this solution while it is on the dialyzer. Dialyze until the dialysate is nearly free from sulfates. The colloidal sulfide is bluish by reflected light and green by transmitted light. It may remain in suspension a few months

A richer blue, but a less stable colloid, is obtained by using only 1 cc. of Rochelle salts. It is well to remove any excess of hydrogen sulfide with a stream of hydrogen If satisfactory results are not obtained vary the amount of Rochelle salts used.

ACIDS

Exp. 35. Silicic Acid.—Dilute commercial water glass to a density of about 1.16. Since carbon dioxide has a coagulating influence on silicic acid, it is well to use freshly boiled distilled water for dilution. Keep in a rubber-stoppered bottle. Pour 75 cc. of this into a mixture of 25 cc. concentrated HCl and 100–150 cc. of water, and dialyze. If it is dialyzed too far a gel may precipitate on the membrane. Rather unstable; easily coagulated by phosphates, etc.

Precipitate a gel of silicic acid, by pouring stronger acid into the water glass and let stand until a gel (jelly) sets Wash the lumps thoroughly with many changes of water and note how little NaOH is required to peptize (see page 18) into the sol form The amount of NaOH required to peptize the gel is far less than the amount called for by chemical reaction.

Read Zsigmondy's "Chemistry of Colloids," page 134.

Exp. 36. Tungstic Acid.—Add a 5 per cent solution of ammonium or sodium tungstate to a slight excess of dilute HCl. Dialyze. Add a little HCl every day or two, until all the alkali is removed. Save a portion of the sol. Evaporate on the water bath until flakes form. These are reversible, that is, they may be redissolved in water Or peptize a freshly precipitated tungstic acid with oxalic acid, and dialyze. Molybdic acid is handled in the same way.

Exp. 37. Stannic Acid.—Zsigmondy dilutes a solution of stannic chloride so that the salt is hydrolyzed almost completely. The gel is then washed by decantation and peptized by a very little ammonia. The excess ammonia is boiled away. Such a sol has been kept for years When precipitated by potassium hydroxide or sodium chloride, the stannic acid goes back into solution on washing out the electrolyte, yet coagulation with acids is irreversible.

CHAPTER IV

DISPERSION METHODS OF PREPARATION PEPTIZATION

DISPERSION methods of preparation are exactly the opposite of condensation methods: larger particles are broken down into smaller. This may be done by grinding, electrical disintegration, the action of various liquids, adsorption of ions, and sometimes by washing out the excess of adsorbed ions from precipitates.

Exp. 38. Bredig's Arc Method.—Make and break an arc under water in a small crystallizing dish, using gold wires run through glass tubes for handles If the water is about 0 002 N with NaOH the results are better Any current of 30–110 volts and 5 to 10 amperes is suitable. When the water is well colored, filter and keep the filtrate Try wires of platinum, copper or silver.

To prove that some oxide is formed, as well as metal, add HCl to some Pt suspension Then pass in H_2S. A dark stain and minute precipitate of the platinum sulfide could not have formed if only the metal were present. Of course, it is conceivable that colloidal platinum might be attacked by hydrochloric acid The more active metals form more oxide

If the gold, made as above, is blue, try heating to see if it turns red. The particles of red gold are smaller than those of blue gold.

PEPTIZATION

Exp. 39.—Heat *dilute* egg-white to opalescence (due to a partial coagulation). Now add pepsin and a trace of hydrochloric acid to "peptize" the protein This experiment illustrates the origin of the term Graham called it "peptonization" because he first used the process to break down protein into peptones (as in digestion) The term now used by all colloid chemists is "peptization."

Glue, gelatin, soap, gum arabic and dextrin are said to be soluble in water. In reality they are merely peptized by water—they are subdivided into particles far larger than molecules. Of course, in hot water some soap is in true solution, and probably a little may be molecularly dispersed in cold water. Even gun

cotton is merely peptized by amyl acetate or by a mixture of alcohol and ether.

At this point it is worth while to read pages 166–171 in Bancroft's "Applied Colloid Chemistry." A quotation from his "Colloid Problems" (No. 38) follows:

"(38) **Behavior of Gum Arabic with Alcohol and Water.**—It is not very easy to peptize gum arabic by grinding with water because the water does not displace the air readily from the gum. If the gum is ground for a moment with alcohol, water then wets it readily. This is surprising because water peptizes the gum and alcohol does not; one would consequently have expected the water to be adsorbed more strongly than the alcohol. By shaking the gum arabic with aqueous alcohol, it should be an easy matter to tell whether the alcohol or the water is adsorbed the more strongly. It is possible that there may be a film of grease on the gum which is removed by the alcohol. It is possible that alcohol displaces the air more rapidly because it adsorbs the air more strongly than does water."

Peptization of precipitates by adsorbed ions is common. Whenever one ion of an electrolyte is more strongly adsorbed than the other, the particles of a precipitate become positively or negatively charged, as the case may be, and repel each other. This disintegrating effect makes for suspension in the colloid form. Clays are kept in suspension in water much longer if a very low concentration of some base is present. Preferential adsorption of hydroxyl ions explains the fact.

Exp. 40. Peptization of Cadmium Sulfide.—Precipitate cadmium sulfide with ammonium sulfide, filter, wash and suspend in water. Pass in enough hydrogen sulfide to peptize the precipitate When suspension is complete boil off the excess of hydrogen sulfide. All sulfides are not peptized by adsorption of an excess of sulfide ion, but the sulfides of cadmium and nickel are—a fact that must be remembered in qualitative analysis.

SILVER HALIDE SOLS

Adsorption of Different Ions

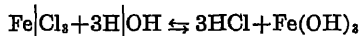
Exp. 41.—Prepare 0 05 N solutions of silver nitrate and potassium iodide From a burette add, while stirring, 20 cc. of the silver nitrate solution to 20 cc of the potassium iodide solution, an equivalent amount. If the precipitated silver iodide does not settle soon, shake the mixture.

To another beaker containing a slight excess of silver nitrate solution, for example, 20 2 cc., add 20 cc. of potassium iodide solution Prepare a series of mixtures, each containing 20 cc. of potassium iodide with 20.5 cc. of silver nitrate or any other small excess of the latter solution. The silver iodide remains in suspension as a positive colloid, having been stabilized by the adsorption of the excess of silver ions. The question is asked at once, " Why is the negative nitrate ion not adsorbed?" This is merely a case of preferential adsorption of silver ions. Yet there is some adsorption of nitrate ions and when the concentration of the negative ions becomes great enough the colloidal silver iodide is discharged and precipitated.

For a similar series add 20 cc. of silver nitrate to varying excesses of potassium iodide. Adsorption of the iodide ion gives the silver iodide a negative charge (How test for this charge?) and thus stabilizes the colloidal suspension. Read Experiments 128, 129 and 130. Washburn states that silver iodide is best peptized by potassium iodide of a concentration of 0 3N.

Exp. 42.—Make colloidal $Fe(OH)_3$ by digesting precipitated and washed $Fe(OH)_3$ with $FeCl_3$. Dialyze Peptization is due to adsorbed ferric ions.

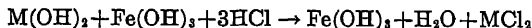
Cautiously add very dilute NH_4OH or $(NH_4)_2CO_3$ to dilute $FeCl_3$. This neutralizes the HCl liberated by hydrolysis and disturbs the equilibrium. Shake until the precipitate is just redissolved Add a little more $FeCl_3$ if necessary to peptize the last of the precipitate.

$$Fe|Cl_3+3H|OH \leftrightarrows 3HCl+Fe(OH)_3$$

It is possible to get a concentration of 14.3 g. of Fe_2O_3 per liter. If the last traces of chloride ions are removed by dialysis the colloid is less stable.

The hydroxides of aluminum and chromium may be peptized by the proper chlorides in a similar manner. The author once attempted to precipitate aluminum hydroxide by adding ammonia to the hot solution of the chloride. It was kept hot too long and could not be filtered. The suspension was set aside and dated. It did not settle for nearly three years.

Freshly precipitated $Al(OH)_3$ is peptized by one-tenth of an equivalent amount of hydrochloric acid.

Exp. 43.—Insoluble hydroxides of the type $M(OH)_2$, when digested with excess $FeCl_3$ of medium concentration and dialyzed yield only colloidal $Fe(OH)_3$. This is due to mass action. Of course the ferric chloride is hydrolyzed.

$$M(OH)_2+Fe(OH)_3+3HCl \rightarrow Fe(OH)_3+H_2O+MCl_2$$

Try $Cu(OH)_2$ as a type. $CuCl_2$ goes through membrane

Exp. 44. Prussian Blue.—Pour a 3 per cent solution of potassium ferrocyanide slowly into a 3 per cent solution of ferric chloride. After a few minutes, filter and wash well. Pour through the filter a 5 per cent solution

of oxalic acid until the precipitate is peptized. Dialyze until no more oxalate ions are found in the dialysate. This is a very stable blue sol and may be kept for coagulation experiments. What is its charge? Compare with Exp. 9.

Exp. 45. Ferric Arsenate.—Peptize *freshly* precipitated ferric arsenate with just enough concentrated ferric chloride. Dialyze for a long time. Peptize another sample with ammonia. For further information, read Jour. Am. Chem. Soc., **40,** 1014 (1918), and **41,** 713 (1919).

Exp. 46.—Fischer and Hertz (Zeitschr. anorg. Chemie, **31,** 352, 1902) showed that when $Cr(OH)_3$ is dissolved in NaOH it is really only peptized. But NaOH will not peptize $Fe(OH)_3$. Yet, if both hydroxides are mixed and treated with NaOH, some $Fe(OH)_3$ is carried into suspension with the $Cr(OH)_3$. Of course, it was adsorbed by the $Cr(OH)_3$. Variations in the relative quantities of the two hydroxides show the limits of the action and throw light on certain analytical results Read Nagel's paper (Jour. Phy. Chem. **19,** 331, 1915).

Use 2 per cent solutions and add NaOH in excess.

$FeCl_3$ cc.	$Cr_2(SO_4)_3$ cc.	
10	50	No precipitate in several days. Dark blue with red-green tint
10	30	Some precipitate. Green above.
20	20	More precipitate. Less green.
30	10	More precipitate.
60	10	Precipitate darker brown. Almost colorless solution
80	10	Brown precipitate. Clear solution.
150	5	Brown precipitate. Clear solution

CHAPTER V

COAGULATION

Many colloids are sensitive to the addition of small quantities of electrolytes, first becoming turbid and then coagulating. Such colloidal suspensions owe part of their stability to the like charges carried by their particles. When these charges are neutralized by ions of opposite charge, precipitation may occur.

Rapid addition of an excess of a precipitating salt often carries a suspension past the precipitating point and gives it an opposite charge with a certain stability. Hardy observed that a colloid was most unstable at the *isoelectric point.* This point was recognized by a failure to migrate in an electric field (cataphoresis) and showed electric neutrality.

Hardy's rule of valence (Schulze's law), that the precipitating power of an electrolyte towards a given colloid depends largely upon the valence of the ion of charge opposite to that of the colloid, is useful in detecting the charge on a colloid.

Hatschek reports an experiment that illustrates this point.

Sol	Charge	Precipitation Concentration in Millimols per Liter		
As_2S_3	–	NaCl 51.0	$CaCl_2$ 0 65	$AlCl_3$ 0.09
$Fe(OH)_3$	+	NaCl 9.25	K_2SO_4 0 20	Still less $K_4Fe(CN)_6$ would have served.

Evidently the precipitating power of the Al^{+++} is hundreds of times as great as that of the Na^+ towards a negative colloid. We might have expected it to be only three times as great. Similarly, the precipitating power (the reciprocal of the concentration) of the SO_4^{--} is about fifty times as great as that of Cl^-, towards a positive colloid. The $Fe(CN)_6^{----}$ is still more powerful.

Svedberg states that the concentration of K^+, Ba^{++} and Al^{+++} required to aggregate particles of As_2S_3 to the same degree stand in the ratio of $1 : \frac{1}{20} : \frac{1}{1000}$.

To determine the nature of the charge, then, on any colloid, we need only compare the concentrations of various electrolytes needed to produce turbidity. For comparison, the different salt solutions must be added at the same rate with the same sort of stirring and the same degree of turbidity secured. Since the precipitation depends on the concentration in the mixture, it is well to add rather small volumes of salt solution to much larger volumes of colloid.

Exp. 47. Precipitation of a Negative Colloid.—Van Klooster suggests an experiment that is worth repeating

Pour 100 cc. each of the following solutions into seven beakers. Add to each 25 cc. of dialyzed colloidal As_2S_3, as a typical negative colloid.

*0 6	milli-equivalents	$AlCl_3$ per liter
1 5		$MgCl_2$
*20.0		$MgCl_2$
60 0		NaCl
*400 0		NaCl
60 0		Na_2SO_4
*400 0		Na_2SO_4

Only the starred (*) concentrations produce clouding and coagulation during the working period. Interpret the results.

Exp. 48.—Using equivalent but very dilute concentrations of NaCl, $BaCl_2$ and $AlCl_3$ for one series, and NaCl, Na_2SO_4 and Na_2HPO_4 for another, measure the minimal precipitating (or clouding) concentrations of these electrolytes towards suspensions of Prussian blue, silver, night blue, chromium hydroxide and ferric hydroxide. From the results state the nature of the charge on each colloid.

From Hardy's rule it may be assumed that HCl, NaCl, KCl, RbCl and other electrolytes with a univalent cation must have the same precipitating power towards negative colloids. This is only approximately true. Ions must be adsorbed before they can discharge colloid particles; therefore, the univalent ions that are most strongly adsorbed by the colloid have the greatest precipitating power. This holds for a similar series of negative ions, etc.

Manufacturing concerns are often anxious to precipitate factory wastes and are given to trusting blindly to alum. This is not a bad guess, for most suspensions in water are negative; hence Al^{+++} with its positive valence of three must be powerful in precipitation. On the other hand, sulfate ions are strongly adsorbed by a large number of colloids, and, being negative, must

tend to peptize a negatively charged aggregate—the opposite of coagulation. Therefore, tests on preferential adsorption are in order in many cases.

H^+ and OH^- are powerfully adsorbed, as a rule; hence the coagulating power of acids and bases is not quite of the same order as that of salts in the same valence series. For example, KCl and KOH have different effects on a negative colloid. The coagulating action of K^+ is partly counterbalanced by the great adsorption, and consequent peptizing action, of OH^-.

Exp. 49.—Compare the precipitating power of equivalent concentrations of KOH and KCl on a suspension of As_2S_3 or of mastic.

So well is H^+ adsorbed that Hardy coagulated a mastic suspension by a much lower concentration of HCl than of KCl. This suggests an extension of Exp. 49.

Organic anions are generally strongly adsorbed; hence, they have high precipitating value on positive colloids. Sodium acetate has ten times as great precipitating power towards $Fe(OH)_3$ as has sodium chloride.

Linder and Picton (Jour. Chem. Soc., **67**, 63, 1895) found that when Ba^{++} precipitated As_2S_3 the barium could not be washed out of the precipitate. Yet, by continued treatment with a more powerfully adsorbed ion (in excess), such as NH_4^+, the Ba^{++} was completely replaced by an equivalent amount of NH_4^+.

Exp. 50.—Divide a suspension of clay or kaolin into two portions. Add a few drops of a solution of alum to one. Does the difference in time of settling suggest a use of alum in water purification? What must be the effect of salt water in the Gulf of Mexico on the suspended soil carried by the Mississippi?

Exp. 51.—Coagulate HgS by the dye, auramine, which is strongly adsorbed. On long standing the colloid becomes crystalline, thus exposing infinitely less surface If the cogulated and washed dye is left in clear water it will finally be seen diffusing away from the crystalline mercuric sulfide. Read in this connection Freundlich's paper, in Zeit. phys. Chem., **85**, 660 (1913).

A splendid paper on the mechanism of coagulation was published by Kruyt and van der Spek in Koll.-Zeit., **25**, 1–20 (1919). A good résumé of this is found in Chemical Abstracts, **14**, 1472 (1920).

Read the coagulation rules of Burton and Bishop (Jour. Phy.

Chem. **27**, 701, 1920). Weiser and Nicholas (Jour. Phy. Chem. **25**, 742, 1921) show that these rules are of limited application.

Wo. Ostwald's thorough study of the colloidal dye, Congo Rubin (Koll Beihefte, **10**, 179, 1919) is a useful contribution to the subject of coagulation.

There is a second class of colloids not coagulated by electrolytes in low concentration. This class includes glue, gelatin, agar, albumin and jelly-like or gummy substances. They can, however, be salted out by high concentrations of ammonium sulfate, for example, or coagulated in some instances by heat or by certain acids. Here we must be careful in making exact general statements. Bridgman (Jour. Biol. Chem., **19**, 577, 1914) states that egg albumin is coagulated at some temperatures by a pressure of 7000 atmospheres.

Exp. 52. Coagulation by Heat.—Heat 20 cc. of dilute egg-albumin to boiling. Some of it coagulates. The coagulation can be completed by addition of 2–4 drops of acetic acid while boiling.

Exp. 53.—With a pipette, cautiously introduce a little albumin solution into an inclined tube containing a few cc. of concentrated nitric acid. At the zone of contact a white layer of precipitated albumin appears This is a very delicate test for albumin.

Exp. 54.—Add saturated ammonium sulfate solution to a dilute solution of albumin. There is no precipitation until an equal volume has been added, and it is not complete until more is added, or until 10 cc. of the mixture contains 6.8 cc of the saturated ammonium sulfate solution.

Solid ammonium sulfate may be added direct to the albumin solution until saturated (below 40°). When water is added to the coagulated albumin (thus diluting the ammonium sulfate) the albumin goes into suspension again. In other words, it is reversible.

An interesting precipitation and crystallization method of purifying albumin is found in Taylor's "Chemistry of Colloids," page 114 (1915).

Duclaux and Wollman (Bull. Soc., Chem. **27**, 414, 1920) by fractional precipitation of an acetone solution of cellulose nitrate with cautious addition of water secured fractions of different viscosities but constant nitrogen content.

Read Bancroft's "Applied Colloid Chemistry," pages 212–223, as a reference for this entire chapter.

Exp. 55. Cataphoresis.—The nature of the charge on suspended particles may be determined by their migration in an electric field (macroscopically or ultra-microscopically). Coehn (Zeit. Elektrochemie, **15**, 653, 1909) used a

large U-shaped tube with two stopcocks of the same bore as the tube itself. The tube was filled with the suspension, stopcocks closed, the ends rinsed and filled with water. After platinum or silver electrodes were hung in the water, the stopcocks were opened and a direct current of 100–200 volts turned on. If the color boundary surface moved slowly to the anode the colloid was negative, etc. Carbon electrodes may be used

A simple device may be prepared from a U-tube with an inlet tube at the bottom and a funnel attached to it with a rubber tube, which may be closed with a screw clamp. In filling, great caution is necessary to prevent mixing of the colloid with the water layer above in each arm of the U. Read Zsigmondy's "Chemistry of Colloids," pages 44–50.

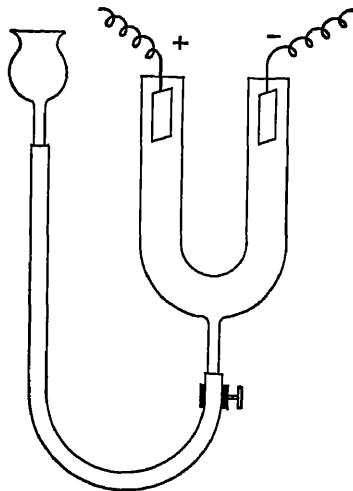



FIG 4.—Cataphoresis.

CHAPTER VI

PROTECTIVE COLLOIDS

Exp. 56. Protected Silver Bromide.—Mix 20 cc. of 0.1 N silver nitrate with 20 cc. of 0 1 N potassium bromide. Set aside until the silver bromide precipitate settles out. To 20 cc. of the same silver nitrate add 2 cc. of 1 per cent gelatin and then 20 cc. of the potassium bromide. Compare the two suspensions as to time of settling.

Exp. 57.—Repeat Bechold's experiment with mastic (Zeit. Phy Chem., **48**, 408, 1904). To 1 cc of a mastic suspension (see Exp. 6) mixed with 1 cc. of 0.1 M $MgSO_4$ add 1 cc. of water. Coagulation will be complete in 15 minutes. Now add 2 drops of 1 per cent gelatin solution to a mixture of the mastic and $MgSO_4$ solution before diluting with water. There should be no precipitation in 24 hours Also try addition of the gelatin directly to the mastic before mixing with $MgSO_4$

Such substances as gelatin, casein, albumin, agar, dextrin, gum arabic and glue interfere with the precipitation of many insoluble compounds. In fact when added in absolutely small but relatively large amounts to a colloidal suspension they "protect" that colloid from the precipitating action of electrolytes, up to a certain point which can be determined accurately. Hence the name, "protective colloids."

In relatively small amounts they cause precipitation if they have the opposite sign. Yet Clayton coagulated several emulsoids by the addition of a relatively small amount of starch paste, although these colloids carried a charge of the same sign as the starch.

Exp. 58.—Prevent the precipitation of a number of the usual compounds so familiar in qualitative analysis by adding a little of any of the protective colloids named above to one of the salt solutions before mixing with the other salt solution. Why do you "destroy organic matter" before proceeding far in analysis of some mixtures?

Exp. 59.—To 50 cc. of colloidal $Fe(OH)_3$ add 2 cc. of 1 per cent gelatin, and compare the volumes of 0.05 N sodium sulfate required to precipitate the colloid with the amounts that precipitate unprotected $Fe(OH)_3$.

Zsigmondy measures protective power by the "gold number." The following quotation is taken from his "Chemistry of Colloids":

"By the gold number we shall understand the maximum number of milligrams of protective colloid that may be added to 10 cc. of gold solution without preventing a change from red to violet by 1 cc. of a 10 per cent solution of sodium chloride, where the change would take place if no protective colloid were added.

"For the determination of the gold number, hydrosols prepared by the formaldehyde method, having particles lying between 20 and 30$\mu\mu$, are the most suitable. The correct degree of subdivision may be known by a faint brownish opalescence in incident light; in transmitted light the solution must be deep red and clear. If the protective effect of the colloid in question is approximately known, it is wise to dilute until a few tenths of a cubic centimeter will prevent the color change. If the effect is quite unknown it should be roughly determined before accurate measurements are attempted."

TABLE I

Colloid	Gold Number	Reciprocal Gold Number
Gelatin and glues	0 005–0 01	200–100
Isinglass	0 01 –0 02	100—50
Casein	0 01	100
Gum arabic, good	0 15 –0 25	6.7–4
Gum arabic, poor	0 5 –0 4	2 –0 25
Sodium oleate	0.4 –1	2 5–1
Tragacanth	2 (about)	0 5 (about)
Dextrin	6–12	0 17–0 08
	10–20	0 1 –0 05
Potato starch	25 (about)	0 04 (about)
Silicic acid	∞	0
Aged stannic acid	∞	0

Exp. 60. Gold Number.—"0.01, 0.1 and 1 cc. of the solution whose protective effect is to be determined (*a*, *b* and *c*) are put into three small beakers and thoroughly mixed with 10 cc of gold ('Zsigmondy's gold') solution. At the end of three minutes 1 cc of a 10 per cent sodium chloride solution is added to each, and the contents well mixed. Assuming that there is a color change in (*a*) but not in (*b*) nor (*c*), the gold number must lie between 0 1 and

0.01. For more accurate determinations, 0.02, 0.05 and 0.07 cc. of the protective colloid should be taken, and the procedure repeated. From the following table it will be gathered that the gold number varies greatly, and can, therefore, be used to characterize this class of substances."

Gelatin is unexcelled as a protective colloid, but Paal has prepared protective material of about the same power by heating albumin with sodium hydroxide. He secures what he calls "sodium lysalbinate and sodium protalbinate." His patents cover the use of this material.

Exp. 61. Paal's Copper.—Add concentrated NH_4OH to freshly precipitated and washed $Cu(OH)_2$ to form a soluble blue complex. This device cuts down the concentration of ions from a copper salt Filter. It is best to add a little less than enough NH_4OH.

Add from 1 to 15 cc. copper solution to 50 cc. of 2 per cent egg albumin. Sols ranging in color from red to blue are obtained.

Paal also advises mixing 20 g. of powdered egg albumin with 20 cc. of 15 per cent NaOH, and diluting to 1000 cc. Heat to boiling and filter. Boil again, adding 1 per cent $CuSO_4$, drop by drop, getting colored sols Dialyze.

As a class, the protective colloids are not very sensitive to electrolytes, and so have emulsoid properties. Some authorities agree with Zsigmondy and Bechold that they act by forming a film around each colloidal particle and thus preventing coalescence of the gold or other particles to be protected. Others hold that protected and protective particles adsorb each other. In any event, irreversible colloids, such as silver, may be evaporated to a solid in the presence of a protective colloid (usually gelatin) and then redissolved in water. Such silver preparations as "collargol" and "argyrol," so much used in medicine, are of this nature.

Exp. 62. Carey Lea's Silver.—Make a solution of 4 g. commercial dextrin and 4 g. pure sodium hydroxide in 100 cc. of water. Add 20 cc. of a 15 per cent silver nitrate solution. In half an hour the dextrin will reduce the silver oxide formed, yielding a reddish-brown sol Precipitate it with 100 cc. of 95 per cent alcohol Let it stand a short time to settle, and then decant the turbid liquid from the silver sediment. This silver readily disperses in a larger volume of water (the alcohol is greatly diluted). When sufficiently diluted, it is clear by transmitted light but greenish black by reflected light. It is very stable. The dextrin acts both as a reducing agent and as a protective colloid

In the commercial manufacture of ice cream, a little gelatin is added as a protective colloid, to give a smooth, velvety taste. The gelatin prevents the formation of gritty little ice crystals.

It is probable that protective colloids are present in many alloys. The lactalbumin of milk has a high protective value, of importance in coagulation. Mother's milk has a higher percentage of lactalbumin than has cow's milk—a significant fact. Jerome Alexander and others advocate the addition of a very little gelatin or gum arabic to cow's milk used in infant feeding. After such addition the coagulated curd formed in digestion is of a looser texture and more readily digested.

Exp. 63. Selenium.—Dissolve 1 g. selenium dioxide in 500 cc. of water To 50 cc. of this solution (hot) add 10 cc of 1 per cent gelatin and then, drop by drop, 60 cc. of hydrazine hydrate (1 : 2000 of water). Keep just below the boiling point for fifteen minutes A beautiful soft peach-pink color appears. Without the protective action of the gelatin the colloid soon precipitates, but when made as above it may be kept for years.

Exp. 64. Color of Photographic Images in Relation to Dispersity of Silver and Initial Nucleation.[1]—As Zsigmondy showed, the initiation of reduction in gold or silver containing reduction mixtures is catalytically accelerated by the addition of colloidal gold, in such a way that, by the addition of gold sols of different dispersity to the reduction mixture, sols of very different dispersity (subdivision) are obtainable

Lüppo-Cramer, in the Kolloid Zeitschrift, drew attention to these experiments and confirmed them for the case of colloid silver action on a silver-reducing mixture in gelatin.

The gelatin is purified, by ten washings with distilled water, from electrolytes, especially chlorides. The colloid silver used is prepared according to Carey Lea's dextrin method and purified by precipitation with alcohol, as in the preparation of colloidal gold.

In each experiment, 100 cc. of 10 per cent gelatin extract are diluted with 400 cc of water; daylight is then excluded, and 20 cc. of 10 per cent silver nitrate are added to the solution at 25°, and the solution is divided into 5 parts of about 100 cc each. Then portions of 0.05 per cent colloid silver are added as follows, 4 cc. of 10 per cent alcoholic hydroquinone being added to each:

Mixture	Color
(*a*) No colloid Ag.	Blue-gray
(*b*) 0 5 cc.	Blue
(*c*) 2 0 cc.	Blue-violet
(*d*) 5.0 cc.	Ruby-red
(*e*) 10.0 cc.	Yellow-brown to yellow (diluted)

The reduction is more rapid, according to the silver added. Results may be observed after thirty minutes. Dilute, if necessary, to see the colors.

The results are still better seen if the sol is finally diluted with an equal

[1] Contribution by S. E Sheppard, Eastman Kodak Co.

volume of 10 per cent gelatin and coated as a thin layer on glass On drying, the color changes observed by Kirchner and Zsigmondy (Annalen der Physik, 15, 573, 1904), Schaum and Schloemann and others with Lippman emulsions, etc., are observed.

On drying →
Yellow ⇄ red ⇄ blue
On moistening ←

The addition of colloid gold in increasing proportions has a similar effect in that an even greater acceleration is produced; but the color stages are the same as for silver additions. Luppo-Cramer points out that not all photographic developers are suitable for the experiments.

From these experiments, it follows that the color of reduced silver passes, with increasing amount of nuclear material from blue → violet → red → yellow. The deduction is simple. In the mixture with most nuclear material, the nascent silver finds the greatest number of aggregation (crystallization) centers. As the amount of silver formable by reduction is *limited*, the *increase* in number of *centers* can only be at the expense of the *size* of *particle*. Since, however, with increasing number of nuclei the color passes from blue → red → yellow, the particle size must increase from yellow → red → blue, which agrees with photographic experience.

CHAPTER VII

SOLVATED COLLOIDS

Wo. OSTWALD classifies colloids as suspensoids and emulsoids. Suspensoids are dispersions of solid particles in a liquid, and emulsoids, he states, are dispersions of a liquid in a liquid. Ostwald divides emulsoids into two subdivisions, the ordinary type of emulsions and the type represented by gelatin, agar, glue, albumin, alkali soaps and silicic acid.

This latter class is distinguished by relatively high viscosity as compared with equal concentrations of suspensoids, and by comparative indifference to low concentrations of electrolytes. The classification given here is challenged by a number of chemists, but it is difficult to draw hard and fast lines. The smaller a drop of liquid the more rigid it is, finally taking on the properties of a solid particle. Some substances may be prepared in both the suspensoid and the emulsoid state. Even barium sulfate has been prepared as a jelly.

The emulsoids of high viscosity are hydrated, or solvated, since other liquids than water may be used. How else could we secure solid jellies with less than 1 per cent of the colloid and over 99 per cent of water, as has been done in some instances? In fact, Gortner prepared a jelly, discussed later in the chapter, containing 99.8 per cent water. By solvation we mean that much of the solvent is firmly held by the colloid. It is not necessary to assume that a compound is formed, but merely that liquid is powerfully adsorbed. It seems to the author that adsorption of water, for instance, may hold layers of water in a condition approaching the solid state. Such adsorption greatly increases the bulk of emulsoid particles, and if by this means the remaining inter-particle space is reduced to capillary dimensions still more solvent may be loosely held.

When viscosity is plotted against concentration, we find that a straight line represents the suspensoids and a curve the emulsoids. The straight line falls well below the curve since at equal con-

centrations the emulsoids are far more viscous than the suspensoids.

Solvated colloids are often called hydrophile (water-loving) or, in general, lyophile. Typical non-solvated suspensoids are called lyophobe.

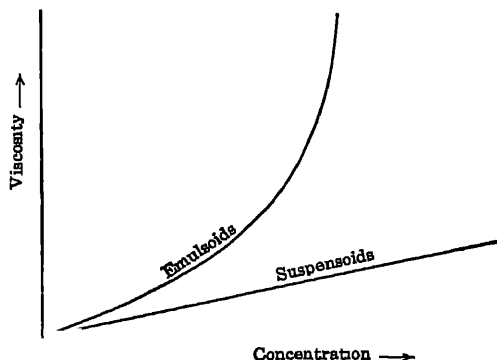



FIG. 5.—Viscosity curves for emulsoids and suspensoids.

Bancroft uses the term gel to include both gelatinous precipitates and jellies. He considers that a gelatinous precipitate is always viscous, contains liquid and settles out at once, leaving supernatant liquid. A jelly, he affirms, does not separate liquid at first, although it may in time.

Without doubt, jellies have a regular structure of some kind, usually requiring a very appreciable time to develop. Gelatinous precipitates form instantly and have but little regularity of structure and but little optical clearness as compared with jellies. Moreover, jellies possess some rigidity and elasticity.

When a suitable mixture of sodium silicate and acid is dialyzed while fresh, silicic acid passes through the membrane for a time, showing that at first the silicic acid is molecular. Later the mixture loses its water clearness and, still later, sets to a solid jelly. This gives a clue to structure. The highly hydrated aggregates are probably roughly spherical, since there is but little chance of orientation with SiO_2. With soap gels, however, and gelatin, too, a filamentous or forked-chain structure is possible and probable. The unlike groups in long molecules may join.

Exp. 65. Solid Alcohol.—Baskerville patented a clever process of making solid alcohol Mix, by tossing from one beaker to another and back again,

90 cc. of 95 per cent alcohol and 10 cc. of a *saturated* aqueous solution of calcium acetate. A jelly sets instantly. Cut out a cube and set fire to it. Let some of the jelly stand in a corked bottle. In a day or two it breaks down into little granules floating around in liquid. This suggests that the original jelly was made up of highly solvated coalescing spheres. Volumes of 85 and 15 cc. will serve as well In fact, some other liquids may be substituted for alcohol Try acetone, methyl acetate, etc. But the solution of calcium acetate must be saturated, beyond question Baskerville stabilizes his jelly by addition of 0 5 per cent of stearic acid

Exp. 66.—Heat 5 cc. of aniline with 95 cc. of water to 100°. There is but one phase. On cooling, minute drops containing over 90 per cent aniline (wet aniline) separate, and a milky emulsion results. Now heat very dilute agar Examine a little as it cools, under the microscope. Minute drops appear If more concentrated agar is used, these minute drops coalesce to a sort of network through which the rest of the liquid can freely pass. Walker states (Physical Chemistry, 231) that these drops are a solution of agar more concentrated than the surrounding liquid Hardy considers a concentrated gelatin jelly as a system of drops of water in a gelatin-rich phase

Martin Fischer considers that hydrated colloid particles separate from water containing little colloid but drops of water containing colloid separate from water containing a much higher concentration of the colloid

Exp. 67. Silicic Acid Jelly.—Dilute commercial water glass ($1Na_2O$: $3.5SiO_2$) of about 1.39 density to 1 : 10 density Pour some of this into an equal volume of N acetic acid. Mix quickly and let stand Note the opalescence preceding the set to a jelly Make 100 cc. of this, cut it out carefully and allow to dry for weeks Observe the changes. In this connection, read Zsigmondy's "Chemistry of Colloids," 137–152, and Bancroft's "Applied Colloid Chemistry," 246–251 An article on "Silicic Acid Gels," by the author of the present volume, in Jour Phys Chem , **22,** 510 (1918), may be useful.

Exp. 68. Vibrating Gels.—Pour water glass diluted to 1 15 density into an equal volume of 6 N HCl. Mix quickly and pour into test tubes or into 100 cc. bottles so that they are only half full. Cork the tubes After a few days, see if the bottles vibrate musically on being held lightly by the top and tapped smartly against wood. Test tubes are rapped on the top with the fingers

Try the same experiment after first greasing the tubes or bottles heavily with melted vaseline Compare these jellies with the above after a week or so All tubes must be corked to check evaporation. See "Syneresis" in the article mentioned below

The pitch of vibration varies inversely as the diameter of the tubes; that is, the gel vibrates as a rigid body, as a suspended bar of iron would do when struck with a hammer The vibrations are transverse. Rigidity is secured by tension. The gel adheres strongly to the glass tube and thus, in attempting to contract, must be under considerable tension Silicic acid does not adhere to a vaselined surface; hence, in the greased tubes, the gel is free to contract and does so, to an astonishing extent. For further details, read the paper by Holmes, Kaufmann and Nicholas, Jour. Am. Chem. Soc., **41,** 1329 (1919)

Exp. 69. Syneresis.—The gels in the vaselined tubes of the preceding experiment separated considerable water, or rather a solution of everything in the gel This spontaneous separation of liquid from gels is called syneresis. All gels exhibit the phenomenon, but it is more extreme in some instances than in others The formation of "curds and whey" from a uniform gel is a familiar instance.

Mix equal volumes of a water glass of 1.12 density and 0.8 N citric acid and let stand in a corked tube to "set" and "synerize."

Further discussion of syneresis may be found in the reference given in the preceding experiment.

Exp. 70. Barium Sulfate Gels.—Von Weimarn states that any very difficultly soluble salt will separate as a gel if made by mixing sufficiently concentrated solutions It is essential that enough of the salt be precipitated in a medium in which its solubility is sufficiently slight This slight solubility may be secured in some cases by addition of considerable alcohol to the aqueous solutions.

Mix equivalent quantities of saturated aqueous solutions of barium thiocyanate and manganese sulfate On long standing, the gel changes to the usual form.

SOAPS

The brilliant work of Martin H. Fischer on the colloid chemistry of soaps has been brought together in a recently published book, "Soaps and Proteins" (John Wiley & Sons). Most of the material in this section has been taken from that book.

Fig. 6 —Water-holding capacities of the palmitates of potassium, ammonium, sodium, magnesium, barium and lead.

Exp. 71.—Determine the water-holding capacity of sodium stearate and of sodium oleate as described by Fischer "Unless otherwise noted, we prepared all our soaps in exactly the same way, by neutralizing a definite weight (one mol) of the pure fatty acid with a chemically equivalent amount

of the hydroxide, oxide, or carbonate in a unit volume (one liter) of water, keeping the whole mixture at the temperature of a boiling-water bath until union between the acid and base had been accomplished. Care was taken to prevent or make good any loss of water from the reaction mixture while in the bath. This gives us a unit weight of pure soap in the presence of a unit weight of water. The mixture was cooled to 18° and the yield of soap weighed. When the entire mixture became gelatinous or solid we considered that all the water had been 'absorbed' by the soap (This statement is qualified elsewhere.) When 'free' water began to appear above the soap, the weight of the theoretical yield of 'dry' soap was subtracted from the weight of the soap as produced, the difference being expressed as per cent of water 'absorbed' by the soap in terms of the weight of the theoretical 'dry' yield.

"Sodium caproate may be taken as the first soap in the series (acetic acid series) to show any water-holding power.

1 mol sodium laurate	holds 4 liters of water
1 mol sodium myristate	holds 12 liters of water
1 mol sodium palmitate	holds 20 liters of water
1 mol sodium margarate	holds 24 liters of water
1 mol sodium stearate	holds 27 liters of water
1 mol sodium arachidate	holds 37 liters of water

"The water-holding power of the oleic acid series is much less. One gram-molecule of sodium oleate holds only one liter of water, as does one gram-molecule of sodium linoleate."

Fig 7.—Water-holding capacities of the oleates of ammonium, potassium, sodium, lithium, magnesium, calcium, mercury, lead and barium One mol of soap to one liter of water.

Exp. 72.—Test part of this experiment. "We added water to 1 g each of carefully dried soaps until, after solution in a hot-water bath, a dry gel was no longer obtained on reducing the temperature of the mixture to 18°. The actual amounts of water taken up by the higher members of the series per gram of soap are shown graphically in Fig. 11."

Exp. 73. Soap with Alcohol.—Add to unit weights of fatty acid the necessary chemical equivalent of 0.5 N sodium hydroxide in absolute alcohol Keep

in the water bath at 75° and add absolute alcohol to each until on cooling to 18° a "dry" gel is no longer obtained. In other words, if the soap-alcohol system remains liquid or shows "syneresis" it is held that its gelation limit has been reached.

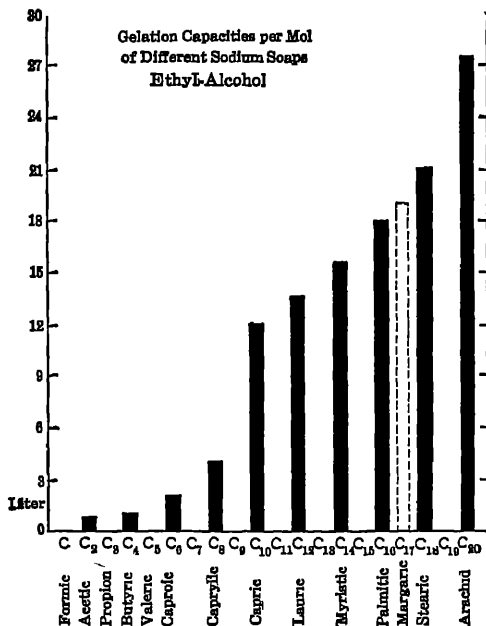



FIG 8.

Exp. 74. Soap with Different Alcohols.—The tendency of the various soaps to yield lyophilic colloids grows (1) with the complexity of the soap in any given series and (2) with the complexity of the alcohol used in the system Examine Figs 18 and 27 in "Soaps and Proteins"

Other solvents can be used, such as the xylenes, ether, benzaldehyde, turpentine, gasoline, heptane and amyl acetate

Gel Structure.—Fischer states that at higher temperatures we have solutions of soap-in-water, while at lower temperatures the system changes to one of water-in-soap. Between these extremes we have various mixtures of solvated soap in soap-water or of soap-water in solvated soap. Examine the interesting diagrams on pages 70–71 of Fischer's book.

The Use of Indicators in Soap Solutions.—Fischer points out the fallacy of the usual indicator method in titrating fatty acid against standard alkali (pages 77–81).

Exp. 75.—Place a drop of phenolphthalein on a sodium stearate/water gel. It remains uncolored. Squeeze the gel to break the structure of the encircling hydrated sodium stearate film. As the enclosed solution of soap-in-water is squeezed out, the spot turns red. Any other soap-water system behaves in similar fashion. Make the gel about 10% soap.

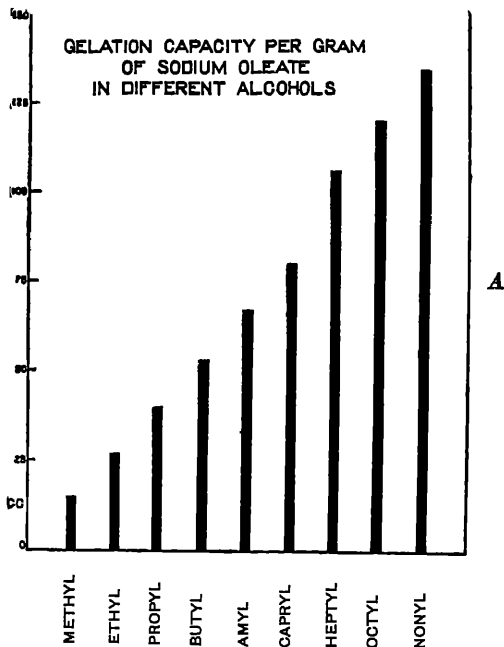



FIG 9

Warm a concentrated sodium oleate solution, which at ordinary temperatures fails to color phenolphthalein. On being warmed, it turns pink. This may be said to be due to increased hydrolysis; yet such a temperature marks a displacement in the system from a solution of the solvent in the soap to one of the soap in the solvent

Add a drop of phenolphthalein to an ordinary (15–30 per cent) "solution" of sodium or potassium oleate in water Is there any color? Now pour water down the side of the inclined tube producing a graded dilution of the soap "solution" What happens?

Read page 88 in Fischer's "Soaps and Proteins" for the discussion of mixtures of soaps, pages 110–116 on the "salting out" of soaps; pages 150–160 on the foaming, emulsifying and cleansing properties of soaps; and pages 163–201 on the colloid chemistry of soap manufacture.

Fischer mentions a number of other liquids, in addition to water and the various alcohols, that solvate soap. The author of the present volume has made many very beautiful jellies using soaps in some of the common lubricating oils.

Exp. 76. Soap-oil Gels.—Dry sodium stearate (any hard white bathsoap will serve) at 90° in an air bath. Make a 2 5 per cent solution in the commercial lubricating oil called "Veedol" or in any petroleum fraction of a high flash point. Heat to 200° if necessary to get a clear liquid Compare with a 0 5 per cent solution of sodium oleate in "Veedol" or in "Arctic" oil. When these solutions cool, solid gels of beautiful clearness are obtained.

McBain and his associates have published valuable papers on the soaps. Read his chapter in the Third Report on Colloid Chemistry published by the British Association. McBain and Martin (Jour. Chem. Soc., **119**, 1369, 1921) determined the degree of hydration of soap curd by salting out the curd in the presence of a known concentration of sodium sulfate and determining the increase in concentration of the sodium sulfate. This increase was due to the fact that soap abstracted some of the water from the solution, in other words, became hydrated.

This method of investigation, although tedious in the case of soap solutions, is worthy of a more general application to the study of solvated colloids.

McBain also believes that the degree of hydration of the fibers of soap curd depends almost entirely upon the vapor pressure of the solution with which it has been in contact, being least for the most concentrated brines. His dew-point method for measuring vapor pressure is given in Jour. Am. Chem. Soc., **42,** 426 (1920) and in Proc. Roy. Soc., **97** [A], 44 (1920)

McBain and Salmon proved that the concentration of OH^- in soap solutions is only of the order of 0.001N. They further state that the conductivity of soap solutions is due to the ionization of the soap itself. In dilute solutions soap is in true solution.

Martin H. Fischer's papers in Science, **48,** 143 (1918) and **49,** 615 (1919) give a brief summary of a number of his findings.

Exp. 77. Pectin Jelly.—The white rinds of citrus fruits, apples and a number of other fruits are rich in a carbohydrate called pectin It may be isolated as a white powder, soluble in hot water

Boil the white peel of any citrus fruit in water Filter and coagulate the pectin with alcohol Wash and dry Make an imitation fruit jelly by boiling a few minutes water containing 1 per cent pectin, 0 5 per cent tartaric acid

and three-fourths of this volume of dry sugar. Fruit jellies need pectin, an acid and cane sugar. Boil until the temperature reaches 105°.

Read: Jour. Ind. Eng. Chem., **12,** 558 (1920), Jour. Phys. Chem., **20,** 633 (1916); Jour. Ind. Eng. Chem., **1,** 333 (1909); **2,** 457 (1910).

C. A. Peters states that when the acid concentration is equivalent to 0.3 per cent sulfuric acid he gets the best gel structure. Less acid is poor, and more is no better than 0.3 per cent. A definite ratio of sugar to pectin is desirable. As the percentage of pectin increases, so does the amount of sugar needed to make the stiffest gel. One volume, or less, of 95 per cent alcohol coagulates a concentrated pectin solution

Di-benzoyl Cystine Gel.—Theories of gel structure must take account of the remarkable di-benzoyl cystine gel recently prepared by Ross Aiken Gortner and Walter F. Hoffman. Brenzinger (Zeit. physiol. Chemie, **16,** 537, 1892) was the first to study this gel.

Cystine is prepared from human hair by hydrolysis with hydrochloric acid. Suspend 2 g. of cystine in 100 cc. of water and add 10 per cent sodium hydroxide until the amino acid dissolves. Then add 10 g. of benzoyl chloride and enough sodium hydroxide solution to make a total of 6 g. Shake vigorously until all odor of benzoyl chloride is gone.

Acidify with hydrochloric acid. The solution sets to a stiff gel which should be broken up by agitation and drained by suction on a Buchner funnel for several hours. Wash the felt of crystals with water. Recrystallize from diluted alcohol. Long, silky needles, melting at 180°–181° are secured.

These needles are insoluble in water and do not contain water of crystallization. They are soluble in most organic solvents.

Brenzinger states that if the alkaline solution from 2 g. of di-benzoyl cystine, as above noted, is diluted to 3 liters and then acidified with hydrochloric acid a rigid gel results, with no free water to pour off. Brenzinger claims a good gel in which only 0.125 of 1 per cent is di-benzoyl cystine and the rest is water. This is startling, considering that the substance has no hydrophylic properties.

Exp. 78.—Gortner's method is different. He dissolves 0.2 g. of pure di-benzoyl cystine in 5 cc of 95 per cent alcohol He adds hot water slowly (keeping the solution boiling) to a volume of 100 cc The beaker is covered and set aside to cool. In two to three hours a transparent gel, as rigid as 5 per cent gelatin, is formed After several days opaque nuclei of stellate groups of needles appear, and syneresis is noticeable.

This gel reminds us of Wo. Ostwald's statement that castor-oil soap forms almost a solid gel in water at 0.1 per cent concentration if a certain amount of alkali is present. Further examples of this sort are detailed by W. Dohle, Koll.-Zeitschr., **12,** 73, 1913.

Cuprimucate Gels.—Pickering (Trans. Chem. Soc., **99,** 176, 1911) prepared and studied a most interesting gel of β-cuprimucate. The precipitate, made by simple double decomposition, was practically insoluble in water. On being heated to 100°, it retained $4H_2O$, but at 120° it became anhydrous.

On the addition of a solution of potassium hydroxide, a blue solution slowly forms. About 1.59 equivalents of the base for each copper atom must be added before any alkalinity is shown. Unless very dilute, this solution turns into a gel in a few minutes. Only when the percentage of copper is 0.5 or less can the gel be filtered, even if hot. It may be boiled without decomposition. Alcohol coagulates the blue solution.

When a weak gel is filtered under pressure it passes through the paper, forming a slightly cloudy filtrate, which gelatinizes again in a day or two. The same cloudy " solution " may be secured by merely shaking a weak gel.

A lump of the gel on a porous tile loses liquid, but a solid residue remains. The gel disintegrated by shaking is completely adsorbed by the porous tile.

Cupriquinate gel is discussed by Pickering in the above reference.

Ceric hydroxide gel is described by Fernau and Pauli (Koll. Zeit., **20,** 20, 1917).

CELLULOSE SALTS

Exp. 79. Saturate concentrated hydrochloric acid at 0° with additional hydrogen chloride This yields a 43 or 44 per cent solution Stir dry shredded filter paper into this solution It dissolves (probably as an oxonium salt). Even acid of 1 209 density dissolves cotton or paper in 10 seconds at room temperatures and more slowly at 0°

This is an example of equilibrium, for in any concentration of the acid below 40 per cent the cellulose does not dissolve The mass action of sufficient hydrogen chloride is necessary to overcome hydrolysis

After fifteen minutes pour a portion of the solution into an excess of water. A colloidal precipitate of hydrated cellulose is produced, due, of course, to hydrolysis of the oxonium salt After thirty minutes pour another portion of the original solution into water The amount of precipitate is much less because of a change to dextrin and dextrose (a mere depolymerization of the

cellulose). After one hour pour another portion into water, and after two hours repeat the experiment. Examine the series of products thus obtained for dextrose, by Fehling's test After two hours' hydrolysis all the cellulose has been converted into dextrose Adapted from Willstàtter and Zechmeister (Ber. **46**, 2401, 1913)

This is the reversal of photosynthesis, by which plants build formaldehyde into sugars and these into starch and cellulose.

A paper by H. E. Williams, "Theory of the Solvent Action of Aqueous Solutions of Neutral Salts on Cellulose" (Memoirs and Proceedings of the Manchester Literary and Philosophical Society, **65**, II, No. 12, 1921) is so striking that it was felt worth while to quote at some length. Not one but many interesting experiments may be devised by the student from the suggestions in the paper. Viscosity may be plotted against boiling points with convincing effect.

"The solution of cellulose in an aqueous solution of a neutral salt is independent of the chemical nature of the salt, but is largely dependent upon the physical properties of the salt solution. For such a solution to dissolve cellulose it must consist of a liquid hydrate—an associated molecular complex of salt and water. But this complex must be of such an order that it has a viscosity above a certain minimum and a positive heat of dilution between well-defined limits.

"Before an aqueous solution can dissolve cellulose it must have a boiling point of 133° C. or over and a viscosity at 100° of 3.3 times that of water at 20°.

"Solution of chemical wood pulp may be obtained in most cases below the boiling point of the salt solution, but in all cases it is necessary to heat the mixture to a minimum temperature varying from 90–133°, depending on the particular salt used. With pure neutral calcium thiocyanate solution boiling at 133°, solution of cellulose may be obtained by heating to 90°.

"Solutions of calcium chloride can be made which have the necessary viscosity and boiling point but they do not dissolve cellulose.

"If one of the necessary preliminary conditions before the cellulose dissolves is the hydration of the cellulose, it is evident that if the water present in the aqueous solution is attached to the salt with too great an affinity it will not hydrate the cellulose and no solution of the cellulose can result.

" Concentrated calcium chloride solution has a very high heat of dilution, therefore it has too strong a dehydrating action to dissolve cellulose.

" Since calcium chloride with so large a heat of dilution was a non-solvent for cellulose, it was thought possible that if a calcium thiocyanate solution could be made concentrated enough, a point should be reached when its heat of dilution would be so great that it would cease to be a cellulose solvent Experimental evidence showed this to be true for a solution concentrated to a boiling point of 150° and over. At this point no cellulose was dissolved even after heating for some time. The addition of a very small amount of water, sufficient to drop the boiling point of the solution to 148° caused the cellulose to dissolve rapidly.

" A solution of sodium thiocyanate fails to become a cellulose solvent because of its low viscosity The addition of other salts that will either not affect, or will not increase the heat of dilution, and at the same time will increase viscosity, should convert the solution of sodium thiocyanate into a cellulose solvent. A very large number of such additions can be made, such as sodium zinc thiocyanate, sodium manganese thiocyanate, aluminium thiocyanate or by dissolving lead thiocyanate in the solution. All these additions increase the viscosity of the solution and at the same time convert the sodium thiocyanate solution into a cellulose solvent.

" Lithium thiocyanate solution does not dissolve cellulose until it is concentrated to a boiling point of 165°, the viscosity being too low for all concentrations below this boiling point; but when the viscosity of the solution is increased by additions of other soluble compounds (manganese, calcium or aluminium thiocyanates or even hexamethylenetetramine, dicyanamide or thiourea), a cellulose solvent may be obtained boiling 30° lower. Each of these solutions has a positive heat of dilution when concentrated.

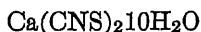
" It is thus seen that there is a definite connection between the boiling point, the viscosity and the heat of dilution of a solution salt, and its solvent power for cellulose.

" Both calcium chloride and magnesium chloride solution when concentrated to the required viscosity have too great a heat of dilution to dissolve cellulose. Additions, therefore, which lower the heat of dilution, and either increase or do not lower the vis-

cosity should convert these solutions into cellulose solvents. This may be accomplished by dissolving mercuric chloride in these solutions to form the double calcium mercuric chloride and the magnesium mercuric chloride respectively.

"If the solutions (any given above) are made acid by a weak acid such as acetic, the cellulose is more readily dissolved and in much greater amounts.

"Both stannic and ferric hydroxides begin to dissolve when a calcium thiocyanate solution is concentrated until the composition of the solution corresponds with the liquid hydrate,

$$Ca(CNS)_2 10H_2O$$

This is the lowest concentration that will dissolve cellulose.

"As an aqueous salt solution having the necessary viscosity and boiling point, but which is not hydrated or only partially hydrated in solution, and therefore contains free water, is a non-solvent for cellulose, it is evident that the combined water plays an important part in the solution of the cellulose, the solution being brought about by means of the combined water, or the capacity of the salt for taking up water. The combination of the salt and water must, however, be of a certain order, that is to say, the water must be bound to the salt between the limits of a maximum and minimum intensity, above or below which no solution of the cellulose can take place on heating.

"A simple and possible explanation of the solvent action on cellulose of these salt solutions, which fulfils the prescribed conditions, may be stated thus: The hydroxyl groups of the cellulose unit link up with the salt complex in place of the water molecules acting in the manner of a substituted water group, thus causing the fibre to swell considerably. The cellulose unit is brought by this means into molecular range with the water molecules combined with the salt. By raising the temperature the union between the salt and water molecules will weaken and they tend to part from the parent molecule. The water thus freed migrates to the cellulose by which it is imbibed, causing further swelling of the fibre, which increases as the progressive hydration proceeds The highly swollen fibre in the gelatinous condition then peptizes, and passes into colloidal solution."

PROTEIN SWELLING

Read the first part "The Argument," in Martin H. Fischer's "Œdema and Nephritis," 3d edition, (John Wiley & Sons). The views there expressed are disputed by some authorities, but they merit careful study.

Exp. 80.—Prepare dry disks of gelatin (page 76). Weigh. Soak in water, 0 02 N or 0.05 N hydrochloric, acetic, nitric and sulfuric acids, and after much swelling has occurred wipe dry with filter paper and weigh again

Exp. 81.—As on pages 61 and 62 ("Œdema and Nephritis"), weigh out powdered blood fibrin, 0.2 g, in narrow test tubes To different tubes add 25 cc. water, 0.1 N hydrochloric, nitric and acetic acids Observe heights of swelling daily. Is there any other influence than that of hydrogen ion concentration on protein swelling?

Exp. 82.—As on page 63 ("Œdema and Nephritis"), try 0 2 g fibrin in

25 cc water
1 cc. 0.1 N HCl+24 cc. water
3 cc. 0.1 N HCl+22 cc water
5 cc 0 1 N HCl+20 cc water
10 cc. 0 1 N HCl+15 cc. water
20 cc 0 1 N HCl+ 5 cc. water

and plot the swelling volume against concentration. Note that bases also cause great swelling. As with acids, there is a definite concentration giving the maximum swelling

Exp. 83.—Make an "artificial kidney," as on page 328 ("Œdema and Nephritis"). Use 0 02 acid to swell the kidney.

Exp. 84.—Immerse a small piece of the dried Achilles tendon of an ox in 0.02 N HCl. In a week a piece 1 cm in diameter will have swollen to a volume of about 30 cc

Exp. 85.—Try Upson's protein swelling with disks of wheat gluten. He works starch out of flour, rolls the gluten to a sheet between glass plates, cuts out disks of about 1 25 g with a cork borer and duplicates the tests above.

Read page 129 of Fischer's book and Jour. Am Chem Soc., **37,** 1295 (1915).

Exp. 86.—The Effect of Salts on Acidic Swelling of Protein.—Weigh out 0.2 g of powdered blood fibrin in each of nine narrow test tubes. In one pour 25 cc. of water, but make the final solutions in all the others 0.02 N in hydrochloric acid and 0.05 M (molar, not normal) in the different salts listed. This gives the comparative effect of different salts in repressing acidic swelling, a matter of some importance for biology and medicine

0.2 g fibrin in water
0,2 g. fibrin in 0 02 N HCl
0.2 g fibrin in 0 02 N HCl+0.05 M NaCl
0 2 g fibrin in 0.02 N HCl+0.05 M Na_2SO_4
0 2 g fibrin in 0 02 N HCl+0.05 M $NaNO_3$
0.2 g fibrin in 0 02 N HCl+0.05 M Na_2HPO_4
0,2 g figrin in 0 02 N HCl+0.05 M NaI
0 2 g. fibrin in 0.02 N HCl+0 05 M NaBr
0 2 g. fibrin in 0 02 N HCl+0.05 M NaCNS

GELATIN

Gelatin is far from "ash free" as purchased, and may be purified by soaking in several changes of distilled water, so that the salts dialyze out. Or it may be placed in water in the middle compartment of a glass box which is cut into three compartments by two porous clay slabs. Electrodes dip into the water of the end compartments. When a direct current is turned on, the electrolytes move out and the gelatin is washed by electric osmose.

A water solution of gelatin may be poured into alcohol and the gelatin precipitated. This coagulum may then be washed and dissolved again in water at 40°, with further purification by reprecipitation.

Jacques Loeb (Jour. Am. Chem. Soc **44,** 213, 1922) prepares ash-free gelatin by bringing it to the isoelectric point and then washing sufficiently with cold water. He states that at the isoelectric point an amphoteric electrolyte like gelatine cannot combine with anion or cation. C. R. Smith (Jour Am. Chem. Soc. **43,** 1350, 1921) also presents a method of making ash-free gelatin. Pauli ("Colloid Chemistry of the Proteins") states that a gelatin studied by him was isoelectric at a H^+ concentration of 1.8×0^{-5} for 1 per cent gelatin.

Exp. 87. Effect of Salts on Setting of Gelatin and Agar.—Hatschek outlines a useful experiment to demonstrate the effect of salts on gelatin and agar. Prepare 250 cc. of 10 per cent gelatin (dissolved at 35°) and an equal volume of 1 per cent agar (dissolved at the boiling point) In each of three 100 cc beakers place enough sodium sulfate, sodium chloride and sodium sulfocyanate (or the potassium salts) to make the 50 cc. of gelatin solution to be added 0.5 N. Of course, only one salt is added to each beaker A fourth beaker contains merely gelatin for comparison A similar series is prepared with agar. The salts are dissolved at 40° in the gelatin and at 100° in the agar Note the order in which the gels set on cooling. What is Hofmeister's series?

Gelatin is very sensitive to treatment. For example, Elliott and Sheppard autoclaved gelatin for four hours at 60 lbs. and secured a liquid with the viscosity of water. Gelatin, heated repeatedly above 60°, loses the power of jellying on cooling; C. R. Smith states that ash-free gelatin does not set to a jelly in cold water but comes out as a precipitate.

Jacques Loeb considers that gelatin forms salts (gelatin chloride, sodium gelatinate, etc.) which form true solutions. His experi-

ments are given in Jour. Biol. Chem., **31,** 343, 1917. His work on the effect of hydrogen ion is found in Jour. Gen. Physiol., **1,** 39, 237, 353, 483, 559 (1918–19). His paper on "The Proteins and Colloid Chemistry" (The Physics and Chemistry of Colloids, a Report by the Faraday Society and the Physical Society of London, Oct. 1920) is a summary of the work described in several previous papers.

The idea that alkalies or acids unite with protein to form new compounds is, by itself, not new. It was early expressed by S. Bugarsky (Pflüger's Arch. **72,** 51, 1898) and has since been confirmed and developed by Hardy, Pauli, Van Slyke, Robertson and others.

Exp. 88. Ferric Arsenate Jellies.—When ferric arsenate (or phosphate) is peptized by a slight excess of ferric chloride and dialyzed, beautiful jellies form on the dialyzer. Removal of the peptizing ions, at a sufficiently slow rate, allows precipitation of ferric arsenate in a hydrated form of the regular structure we call a jelly. For details, see Holmes and Arnold, Jour. Am. Chem. Soc., **40,** 1014 (1918); Holmes and Fall, *ibid*, **41,** 763 (1919).

Exercise.—From the experiments in this chapter develop a classification of the ways in which jelly structure may be obtained.

A useful chapter by Stocks on several common solvated colloids is found in the First Report on Colloids (46–78) issued by the British Association.

CHAPTER VIII

SURFACE TENSION

THE surface film of a liquid is in a state of tension due to the unbalanced attractions between molecules at the surface as compared with those which are entirely surrounded by other molecules. The molecules in the surface layer of liquid are attracted only downward and sideways, not upward, since there are no liquid molecules above them. Consequently, the surface molecules act as if they formed a tightly stretched but elastic skin over the surface of the liquid. As a result of this *surface tension*, every liquid tends to assume the spherical shape because the sphere, of all shapes, has the least surface.

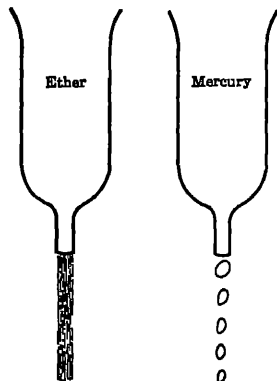



FIG. 10—Liquids of low- and high-surface tension.

When a liquid wets the walls of a glass capillary tube, the surface is concave and the liquid rises to a height inversely proportional to the diameter of the tube. The unit surface tension is the tension across a line 1 cm. in length.

"If we denote the value of surface tension by γ," writes Findlay, "and by h the height in centimeters to which a liquid of density s rises in a tube of radius r cm., we obtain the expression

$$\gamma = \tfrac{1}{2}hrsg$$

where g is the value of gravity (981 dynes). We then obtain the value of the surface tension in absolute units (dynes per centimeter). The value of γ is dependent on the nature of the liquid and also on the temperature, rise of temperature being accompanied by a decrease of the surface tension."

By the *drop weight* method we determine the weight of a drop of liquid falling freely from the end of a tube.

Or, with Traube's stalagmometer, we count the number of drops formed by a given volume of liquid. From this we can calculate surface tension. For working directions on the capillary rise method and drop weight method, read Findlay's "Practical Physical Chemistry," pages 89–96 (1914).

The stalagmometer is used to determine surface tension of liquid against *air*, but it may be modified to determine surface tension of one liquid against another. In connection with the chapter on Emulsions we shall find this method very useful. Surface tension is not absolutely inversely proportional to the drop number, but it approximates it well enough to make the method worth while.

Harkins (Jour. Am. Chem. Soc., **41**, 520, 1919) determines surface tension with great accuracy and discusses the theory in detail

FIG. 11 — Donnan pipette (improved by Shorter)

Exp. 89. Use of Donnan's Pipette.—Since surface tension lowering is a factor in emulsification, it is of importance to have a method of measuring the change in surface tension between the two liquids to be emulsified. Donnan devised a pipette with which he allowed a definite volume of liquid *A* to run into liquid *B* or into liquid *C*, etc. The lower the surface tension between the two liquids the greater the number of drops Therefore, merely counting the number of drops gives an approximate measure of surface tensions Shorter's modification of this pipette is very useful

Use a capillary tube of 1 mm bore Blow a bulb at *C* holding 1 or 2 cc To regulate the flow, a short piece drawn down to a hair opening at *A* is connected to the pipette by the rubber tubing *B*. The tip *D* is shown magnified at *E*.

Drops sometimes widen at their point of attachment, changing their size By using heavy glass and grinding the end level, it is easy to detect such accidental distortion and to discard the reading Readings are taken between *F* and *G*, marks on the tube Determine the drop numbers of benzene (or any hydrocarbon) against water, 1 per cent sodium chloride, 1 per cent sodium oleate, 1 per cent sodium hydroxide and 1 per cent sulfuric acid. Draw conclusions

Drop Spread.—The surface tension of mercury is 436 (at 15°), of water 70.6 (at 20°), and of ether 16.5 (at 20°). Which of these

liquids should give the flattest, thinnest drop on a glass or porcelain plate? Test your opinion. Wo. Ostwald observes that a glass tube may be drawn out to a tip of such aperture that ether runs through it in a stream while mercury runs through in droplets. Explain.

Exp. 90.—From a height of 1 cm. (for example) let 0.5 cc. of water fall from a burette on a thoroughly cleaned glass plate. Measure the "drop spread" in millimeters as soon as the maximum width of the spot is reached. Compare with the drop spread of a 1 per cent solution of sodium oleate. This is a rough method of measuring surface tension, useful at times if precautions are taken to prevent evaporation.

(The following is taken from P. Lecompte du Nouy by the author's permission from The Journal of General Physiology, **7**, 521, 1919.)

"The importance of the action of surface tension in biological phenomena is well known, but all the techniques of measurement are either complicated (static methods: capillary undulations, drop rebounding, capillary jets, rebounding jets), or long (drop method); and it is desirable to have a simple apparatus by means of which the surface tension, and especially the variation of surface tension of a given liquid, can be readily measured, with sufficient accuracy. For this reason the apparatus to be described has been designed. There is no new principle in it; it is based upon adherence of a ring, or of any other design, to the liquid (Weinberg). It is simply a torsion balance, but instead of measuring the tension by means of weights (which is time-consuming, and makes two readings necessary), it makes use of the torsion of the wire to counteract the tension of the liquid film and to break it. A single reading on a dial indicating the degree of torsion of the wire gives a figure, which, if the apparatus has been previously standardized with water, gives the surface tension of the liquid by a simple proportion. From the fact that the torsion of the wire for water, which has the highest surface tension, is only 72°, we can assume that, within these limits, the strain of the wire is proportional to the angle of torsion, so that no table of correction is needed."

The instrument consists essentially of a stand provided at the top with a fine steel wire stretched between end supports. One end of the wire is tightly clamped, the other being attached to a worm wheel controlled by thumb-screw (*b*). To the worm

wheel is also attached a pointer (*a*) which moves over a metal scale graduated in degrees. To the middle of the wire is clamped a hollow, light aluminum lever (*d*) with a small hook in the outer end. A stirrup attached to this hook carries a carefully made loop (*h*) of platinum-iridium wire with a periphery exactly 4 cm. in length.

"The watch glass, or other vessel containing the liquid whose surface tension is to be determined, is placed on the platform (*g*) and carefully raised by means of the adjusting screw until the platinum loop has made contact with the liquid. The pointer (*a*) having been previously set at zero, the torsion of the wire is gradually increased by means of the thumb-screw (*b*) controlling the worm gear, until the loop of wire tears loose from the liquid. The number of degrees is then read from the scale and by a simple calculation is converted directly into dynes per centimeter.

"This instrument provides the most rapid and direct-reading device for measuring surface tension which has yet been produced. The method is simple, yet capable of the highest degree of precision in measurement. This is the only device by which the surface tension of colloidal liquids can be accurately determined. A feature of special importance is the fact that a complete determination can be made in from fifteen to thirty seconds, and results can be duplicated over and over with perfect agreement. Another interesting feature of the instrument is the small amount of liquid required, 1 cc. being sufficient. This permits a wide use, particularly with biological fluids, which are usually available only in small quantities. The instrument can be readily and quickly standardized by the use of pure water at 20° C.

"The first precaution to take is to clean thoroughly the platinum wire (*h*), by flaming it, or by washing it in a solution of 10 cc. of saturated potassium dichromate solution in 990 cc. of sulfuric acid, and rinsing it carefully under a flow of ordinary tap water, running from the stopcock, unless very pure distilled water contained in clean and greaseless bottles can be provided.

"The same thing must be done with the watch glass, or the beaker used for containing the liquid, the surface tension of which is to be measured. It is advisable to allow them to boil for five minutes in the above-mentioned solution, in order to remove the slightest trace of grease

"These parts are then put in place, without being touched

with the fingers; that is, the platinum loop (*h*) hooked to the lever (*d*), and the watch glass containing the liquid on the table (*g*).

"The zero is now determined. For this, the needle (*a*) is brought by means of the knob (*b*) just in front of the point 0 on the dial. Then, by means of the adjusting screw (*f*), the torsion of the wire is modified until the lever (*d*) is just above the resting platform (*e*), the distance between them not exceeding a small fraction of a millimeter; for instance, the thickness of a piece of very thin paper. The screw (*c*) being fixed in position, one will

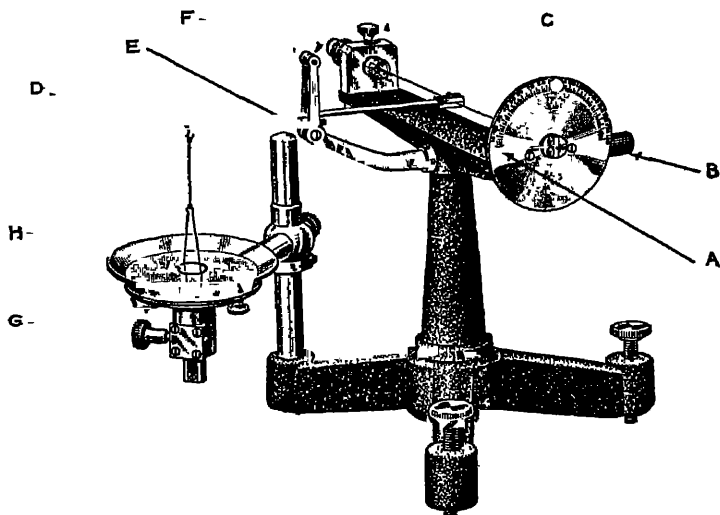



FIG. 12.—Du Nouy surface tension apparatus

observe that an imperceptible movement of the knob (*b*) will bring the lever in contact with the platform (*e*), practically without changing the reading on the dial. The apparatus is now ready for use.

"The table (*g*) is raised slowly by means of the adjusting screw until the liquid touches the platinum ring (*h*). One must be sure that a perfect contact exists. Then by turning the knob (*b*), the torsion of the wire is controlled, and one keeps on turning until the ring is suddenly separated from the liquid, by the tearing off of the film. The reading is made. One can rapidly check this reading by one or two others.

"The figure read being carefully noted, the liquid is lowered

and the standardization takes place, as follows: A small piece of clean paper is cut in such a shape that it can easily be slipped upon the platinum ring (*h*), in the stirrup, after it has been weighed. Then weights are added on top of it, until the lever is forced down to its horizontal position, not quite in contact with the platform. It is now obvious that the sum of the weights plus the weight of the paper represents exactly, in grams, the strain of the wire. This being determined, the strain of the liquid film which was counteracted by the torsion of the wire is known. This is, in fact, a measure of the surface tension of the liquid, according to the definition. But, as surface tension is conventionally expressed in *dynes per centimeter*, the number of grams must be multiplied by 981, and this figure divided by the length of the circumference of the ring, that is, 4 centimeters, in order to have the number of dynes for every centimeter. It must also be observed that not only one, but two films acted on the ring, one outside, and one inside. It is necessary, therefore, to divide again by *two*. The formula then becomes:

$$A \text{ (surface tension in dynes)} = \frac{M \text{ (in grams)} \times 981}{2 \times 4}$$

Or generally:
$g = 981$, $L =$ length of platinum wire, in centimeters

$$A = \frac{Mg}{2L}$$

Example: Water at 25° C.

Grams necessary to bring lever down	0.610
Weight of paper	0 018
Total weight	0 628
then:	0 628 × 981 ÷ 8 = 77 dynes

"Once this standard measurement is obtained, it is compared with the reading on the dial, as for instance, 72°. Then any readings on the dial, multiplied by the ratio $\frac{77}{72}$ will give the surface tension, in dynes, of any liquid tested as before. In order to save time, we suggest that the slide rule be used, which will obviate any calculations. By simply setting 72 under 77, all figures of the upper scale of the rule will represent the surface tension, in dynes, corresponding to all figures read on the dial, on the lower scale."

Exp. 91.–With the Du Nouy apparatus, measure the surface tension of water, of a 1 per cent aqueous solution of night blue, of alcohol and of a 1 per cent alcoholic solution of night blue.

Night blue is colloidally dispersed in water and molecularly dispersed in alcohol Draw your own conclusions With the same apparatus learn if there is any difference in the surface-tension lowering caused by suspensoids and emulsoids.

J. Willard Gibbs (Scientific Papers, I, 219) taught that any dissolved substance lowering surface tension must concentrate in the surface layer. This important statement applied to true solutions; yet it is a fact that some colloids concentrate at the surface far more then called for by the formula. The surface tension of a fresh solution is often very different from that of an older solution. In some instances it requires appreciable time to reach equilibrium between the change in surface tension and the osmotic pressure difference of surface film and mass of solution.

SURFACE PHENOMENA CONNECTED WITH SOAP SOLUTIONS[1]

Change of Surface Tension of Soap Solutions with Time

Object.—Simple method for determining surface tension of soap solutions and *variation with time*

Exp. 92. Procedure.—Make up a dilute solution of sodium stearate (1 part in 15,000) by diluting the stock solution containing 0 001 gr /cc with the required amount of distilled water. Pipette a portion into a watch glass and immediately measure surface tension by Du Nouy surface tensimeter (or a home-made apparatus similar to this). Continue the readings once every minute for half an hour Repeat with sodium oleate. Record *variations with time* and explain them

Surface Films on Soap Solutions.

Object.—To demonstrate the presence of a surface film on soap solution

Exp. 93. Procedure.—Allow a dilute solution of sodium stearate, on the surface of which talc has been dusted, to stand several minutes in an open dish. Dip a fine glass point into the surface, observing the movement of the surface as the point is moved to and fro Repeat the above experiment, using sodium oleate Compare results

[1] Contributed by Leon W. Parsons and R. E. Wilson, of Massachusetts Institute of Technology.

We quote from No. 182 of Bancroft's "Two Hundred Colloid Problems."

Stabilization of Foam. "To get a foam the only essential is that there shall be a distinct surface film; in other words, that the concentration in the surface layer shall differ perceptibly from that in the mass of the liquid. All true solutions will, therefore, foam if there is a marked change of surface tension with change of concentration, regardless of whether the surface tension increases or decreases. All colloidal solutions will foam if the colloid concentrates in the interface or if it is driven away from the interface. To get a fairly permanent foam the surface film must either be sufficiently viscous in itself or must be stabilized in some way. This can be done by introducing a solid powder into the interface.

Exp. 94.—" Solutions of aqueous alcohol, acetic acid, sodium chloride and sulfuric acid all foam when shaken; but the foam is unstable. Soap solutions foam when shaken and the foam is, or may be, quite stable, owing to the viscosity of the soap film. With saponin the surface film is even more stable. If we add to aqueous alcohol some substance like lycopodium powder which goes into the interface, we get a stabilized foam We can do the same thing with aqueous acetic acid by adding lampblack. The presence of enough of a finely divided solid in the interface will make the film so viscous that the foam will be quite stable Grease will help stabilize a foam in some cases and it has been claimed erroneously that the foaming of sulfuric acid solutions is due to grease."

R. E. Wilson and Leon Parsons believe that stable foams are produced only when the surface layer has the properties of a plastic solid rather than of a viscous liquid.

"Surface Tension and Surface Energy" by Willows and Hatschek is a book of 80 pages published (1915) by Blakistons.

CHAPTER IX

EMULSIONS

BEFORE performing the experiments of this chapter read most of the references following:

W. D. Bancroft, Applied Colloid Chemistry, 161, 260–273; Martin H Fischer, Fats and Fatty Degeneration, 1–16 (John Wiley & Sons); Emulsions, Jour. Ind. Eng. Chem., **12,** 177 (1920); Pickering's paper, Jour. Chem. Soc, **91,** 2001 (1907); Clowes' paper, Jour. Phys. Chem., **29,** 407 (1916).

There are conflicting views in these various articles, but they are all stimulating.

Emulsions are, of course, dispersions of minute drops of one liquid in another. Two mutually insoluble liquids may be emulsified by mechanical agitation, but they soon separate into two layers of the original liquids. Such emulsions are not stable when they contain more than 1 per cent of the dispersed phase. Poor emulsions of this type may be secured by pouring 10 cc. of a 1 per cent solution of any oil in acetone (or alcohol) into 1000 cc. of water. Stable emulsions of two pure liquids cannot be made. A third substance, usually colloidal, is necessary to stabilize emulsions. This is often present as an unsuspected impurity. The exact manner in which this third substance, the "emulsifying agent," functions is in dispute. The different theories are illustrated in the following experiments.

Exp. 95. Soap as Emulsifying Agent.—Shake together oil (kerosene will do) and water A temporary emulsion forms Now shake 20 cc of oil with 60 cc. of 1 per cent sodium oleate Let it stand. The soap has lowered the surface tension of the water, probably concentrating as a film around each oil globule, and it has "bound" all the water. These points represent three theories of emulsification All may apply in certain cases In other cases a single influence is predominant

A "cream" rises to the top in soap emulsions This cream is much richer in oil than is the liquid below. To prove this, separate the two layers with a pipette and break the emulsions with any acid This liberates free

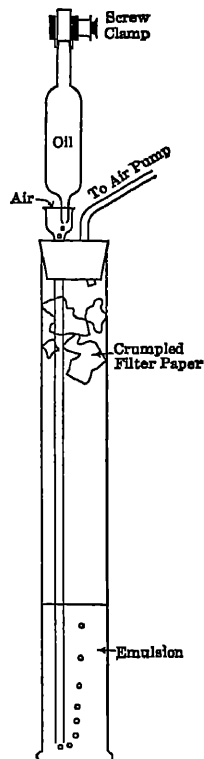
fatty acid which has no emulsifying power. Compare volumes of the oil layers separating.

Agitation is necessary to break at least one liquid into drops. Briggs (Jour. Phys. Chem., **24**, 120, 1920) insists that intermittent shaking is better than continuous shaking. Agitation may be secured by hand shaking, shaking machines, egg-beaters, mortar grinding or by air stirring as with Hatschek's device, Fig. 13 The flow of oil from the pipette is regulated by a screw clamp, so that 50 cc. of kerosene would be delivered in thirty minutes This oil is dropped into a long-stemmed thistle tube which admits air at the same time The lower tip of this thistle tube (reaching nearly to the bottom of the cylinder) should be only 1 mm in diameter, for the best results The rubber stopper in the top of the cylinder fits tightly, so that the suction from the air pump can draw air and oil down the thistle tube The cylinder contains one-fourth of its volume of soap water (usually 1 per cent sodium oleate) To prevent froth being carried over, a few sheets of loosely crumpled filter paper are pushed into the upper part of the cylinder Before the apparatus is set up, the thistle tube must be wet with oil. To do this, pour a little oil through the tube, while tilting and rotating it

FIG. 13 —Hatschek's emulsifier

A counter-current beater is very useful in agitating liquids It consists of two propeller blades attached to the same shaft so that one is inverted, each throwing a current of liquid against the other Cut a slot in a brass shaft and solder in two copper blades which had previously been bent to shape The whole device should be nickel-plated The shaft may be set in a rubber tube as a bushing.

Exp. 96.—With *Hatschek's emulsifier*, see if you can make a 90 per cent emulsion of cotton oil in 1 per cent sodium oleate or in potassium oleate

Exp. 97. Gelatin as an Emulsifying Agent.—Use any good gelatin, although we prefer "Difco," made by Digestive Ferments Co. of Detroit Difco gelatin has an ash content of 1.1 per cent and sets to a jelly at a concentration of 1 1 per cent or less. Make a 0 4 per cent solution of gelatin in water at 40°. Place 10 cc in a 125 cc oil sample bottle and add 5 cc. of kerosene at a time, with intermittent shaking. It is possible to add a total of 30 cc. or more of oil, making a 75 per cent emulsion. Holmes and Child, J Am Chem Soc, **42,** 2049, 1920

Emulsion Theories.—Plateau and Quincke believed that surface-tension lowering by the emulsifying agent was its most important function. Since the alkali soaps lower the surface

tension of water greatly, they have been favored as aids to emulsification. Yet Martin Fischer holds that the alkali soaps are effective rather because they are solvated colloids and thus "bind" the water. Read "The Argument," pages 1–15, in his "Fats and Fatty Degeneration," for further statements on his theory.

In the more common type of emulsions drops of oil are dispersed in water (oil-in-water) yet the opposite type is well known. Drops of water may be dispersed (with the aid of the proper emulsifying agent) in oil forming water-in-oil emulsions.

The heavy-metal soaps are not good emulsifying agents for the oil-in-water type. Yet they are good emulsifying agents for the water-in-oil type, Fischer holds, because they are not hydrated to any marked extent. Gum arabic, gelatin, albumin and all the solvated colloids are useful emulsifying agents. We have used gelatin in the previous experiment with good results. The normally present proteins of egg yolk keep the 30 per cent of fat of the yolk in emulsified form. Still more fat may be added as when mayonnaise is made. Acid casein and alkali casein both hydrate well, and so yield good emulsions of oil-in-water. But when either is exactly neutralized, neutral casein, a slightly hydrated substance, results and the emulsion breaks. Potassium soaps are better emulsifying agents than sodium soaps, because their films are softer at room temperatures.

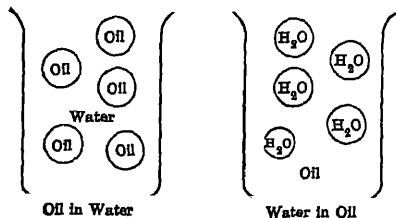



FIG 14.—Emulsion types

Pickering made good emulsions of oil-in-water by using basic copper sulfate as the emulsifying agent. Thus he reasoned that oil globules, or drops, could be kept apart by small discrete particles of an insoluble substance. It is true in a few instances, but his theory is not of general application. We give his experiment below.

Bancroft considers that a tough elastic film around each oil drop is necessary to stability. He thinks that the good emulsifying agents are those colloids that are concentrated at the liquid-liquid interface by strong adsorption. Froth concentration of a dye, as outlined below, throws light on this theory.

Exp. 98. Mayonnaise.—Beat the whole egg to a froth and then add cottonseed oil (or olive oil), at first drop by drop and then a few cc. at a time, up to 100 cc Of course, the egg-beater or other stirring device is used almost constantly. Now add 2 cc. of strong vinegar, more oil up to 100 cc and finally the rest of the vinegar Salt (5 g) with other seasoning is added later in the process If oil is steadily worked in until the total volume of oil used is 250 cc., a very good mayonnaise results. The yolk of egg may be used as the emulsifying agent. More than 15 cc. of vinegar may interfere with the proper consistency of the mayonnaise, or make it "crack" because the acid dehydrates some of the hydrated protein colloids (globulins) But more is often used to suit the taste of the cook

Exp. 99. Pharmaceutical Emulsions.—Oesper (Jour. Ind Eng Chem, **9,** 156, 1917; *ibid*, **9,** 966, 1917) observes that some pharmacists, instead of adding the oil last in their acacia (gum arabic) emulsions, start out with a nucleus, such as 4 parts olive oil (cottonseed oil is cheaper), 2 parts powdered acacia and 3 parts water. This is ground in a mortar until it "takes" to a cream and may then be diluted (grinding) with more oil or water. In some instances it "takes" better after standing a few hours

Exp. 100. Pickering's Emulsions.—Churn 50 cc of a petroleum distillate heavier than kerosene into a mixture of 134 cc limewater and 1 g $CuSO_4 \cdot 5H_2O$, dissolved in as little water as possible, adding oil all at once Here a plastic film of separate, minute solid particles of basic copper sulfate covers each oil drop

Read Jour. Chem. Soc, **91,** 2001 (1907) for further directions and comment.

Exp. 101. Adsorption Films.—Peptize air-dried cellulose nitrate (11 per cent nitrogen) by a mixture of 1 part of amyl acetate and 3 parts of benzene, making it about a 2 per cent solution Pour enough of this into a small beaker to give a layer nearly 1 cm deep. With a pipette, add a very large drop, or globule, of water and watch it for a few minutes A visible film quickly forms Gently tilt the beaker and distort the drop by rolling it around Wrinkles in the film demonstrate its toughness and elasticity. This film of cellulose nitrate has lowered the surface tension of its solvent and thus concentrated at the interface Similar films may form in other instances but may lack visibility because of an equality of indices of refraction of all the substances present. This experiment supports Bancroft's theory, in this instance, at least. If it fails use much more benzene.

Froth Concentration of a Dye.—Another example of the concentration of dissolved substances at surfaces is found in the frothing of an aqueous solution of methyl violet. Here the interface is between water and air. Miss Benson (Jour Phys Chem., **7,** 532, 1903) first demonstrated that such a froth of aqueous amyl alcohol showed a higher concentration than did the solution beneath; but we give experimental details from Kenrick (Jour. Phys. Chem., **16,** 517, 1912).

Exp. 102.—Shake a solution of 0.08 g of methyl violet in 300 cc. of water in a 1000 cc. separatory funnel. After a good froth is secured let stand about four minutes. Drain off the clear liquid In about four minutes longer, the foam in the funnel will subside to liquid. If not, add a drop of ether to break the froth Drain off 1 cc. and dilute with 20 cc of water. Also dilute 1 cc of the original solution with 20 cc of water. Compare the two samples in in depth of color before the lantern. The solution prepared from the foam is darker than the other, thus showing a greater concentration of dye.

Concentration at the Interface.—The following is quoted from a pamphlet issued by the Sharples Specialty Co :

" When crude corn oil is agitated with hot water a thick white emulsion forms. When this emulsion is passed through the Sharples Super-Centrifuge at a moderate rate of flow, some of the oil separates and is discharged as a clear yellow oil. The rest of the emulsion is discharged in a highly emulsified condition.

" The oil separated in this way will not form a stable emulsion when again agitated with hot water, because the emulsifying agent has been extracted. But when the discharged emulsion is broken by any chemical means the separated oil is easily emulsified again."

This seems to be a good illustration of concentration of the emulsifying agent at the oil-water interface.

A Comparison of Theories.—Harkins, Davis and Clark (Jour. Am. Chem. Soc., **39**, 541, 1917) think that the best emulsifying agents have long molecules with a polar active group at one end of the molecule. (Polar groups such as COOR—COOH.) Langmuir (Jour. Am. Chem. Soc., **34**, 1848, 1917) believes that the organic groups strike inward into the fatty globules, while the COOH, SO_3H, etc., are outside in the water phase. There is probably no real clash between the solvated colloid idea and the suggestion of adsorption films around drops of the dispersed liquid. If there is not enough colloid to be uniformly distributed in the liquid that peptized it, some of the adsorption film will be peptized back into the liquid. Doubtless the film is essential; but its existence in the " right physical condition " depends upon the peptizing action of the one liquid on the film. Solvated colloids are the best emulsifying agents.

Having studied the action of cellulose nitrate as an emulsifying agent (Jour Am. Chem Soc. **44**, 66, 1922) the author believes that the ideal film for an emulsion must be one that forms readily and comes quickly to an equilibrium between the peptizing

action of the one liquid and the precipitating action of the other. It should be tough and elastic and should change little with age. Such a film on the solvent side should be gelatinous and swollen with that liquid. On the side of the second liquid it should be coagulated, not to the point of brittleness, yet should be "wetted" somewhat.

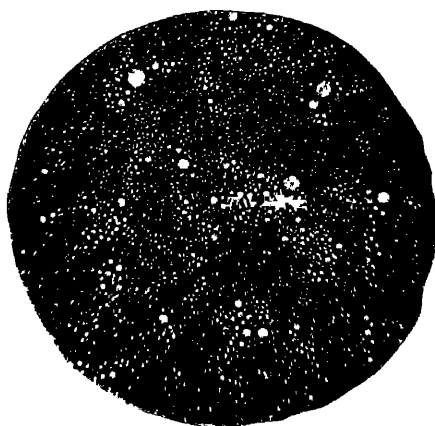
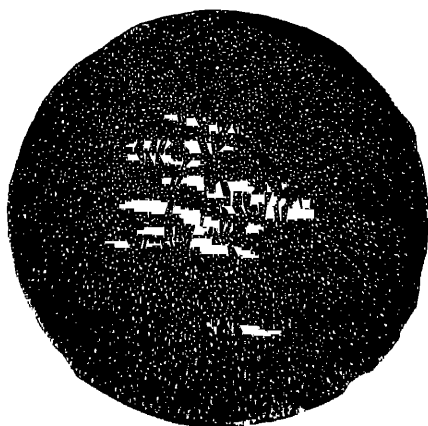
Exp. 103.—Dissolve 0.3 g gelatin in 40 cc. of water and then add enough Na_2SO_4 to make it half-molar On shaking, a froth, stable several days, should result The same amount of gelatin in 40 cc. of half-molar NaI yields a temporary froth on shaking yet it has a lower surface tension against

Fat globules in an ice cream mixture (×200).

Fat globules in a homogenized ice cream mixture. (×200)

Fig. 15

oil as shown by the Donnan pipette. Therefore the gelatin must have been coagulated sufficiently by the Na_2SO_4 to give a higher surface viscosity to the film. The NaI peptizes gelatin making the particles too small to give such high surface viscosity.

Exp. 104. The Use of Donnan's Pipette in Emulsion Studies.—With the Donnan pipette drop kerosene into water, into 1 per cent sodium oleate; into 0 5 per cent sodium hydroxide, into a mixture containing 1 per cent of soap and 0 5 per cent of sodium hydroxide Drop cotton oil into water; into 0.5 per cent sodium hydroxide. Count the drops for equal volumes of oil and draw your conclusions Remember how soaps are made. Review the use of this pipette in the chapter on Surface Tension

Exp. 105. Creaming.—Soap emulsions "cream" as does milk. Creams rise or sink according to the densities of the two liquids If the two liquids have the same density they never cream Mix cottonseed oil and

CCl_4 (at some definite temperature) until a drop released from a pipette neither sinks nor rises in the soap water used Make an emulsion and it will not cream.

Emulsions containing drops sufficiently small never cream Homogenized milk illustrates this point.

WATER-IN-OIL EMULSIONS

The ordinary emulsions, and those previously discussed in this chapter consist of drops of " oil " (meaning any liquid insoluble in water) dispersed in water. All of these were made by the use of a colloid emulsifying agent peptized by the water. Yet if a colloid peptized by the " oil " and not by water is used, the phases are reversed and the water is dispersed in drops throughout the oil. For example, the alkali soaps are more soluble in water than in oil, hence they always aid in formation of the usual type of emulsions, oil-in-water. On the other hand, the soaps of the alkaline earths and heavy metals are generally more readily peptized (hot) by oils than by water, and thus aid in the formation of the unusual and less stable type of emulsions. It may even be said that any substance more readily " wetted " by one liquid than by another favors dispersion of the second liquid in the first. Clowes (Jour. Phys. Chem., **20**, 407, 1916) considers that the determination of phase depends upon the convex or concave bending of the liquid interface as influenced by surface-tension lowering caused by the emulsifying agent. Newman's work with the oleates of magnesium and calcium (Jour. Phys. Chem., **17**, 501, 1913) shows the influence of the two classes of soaps.

When " Nujol " is shaken with water containing about 1 per cent sodium oleate as the emulsifying agent, the oil is dispersed in the water. Also, when a " Nujol " solution of a suitable emulsifying agent, such as magnesium oleate, is shaken with water, it is the water that is dispersed in the oil. Newman (Jour. Phys. Chem., **18**, 40, 1914) observed that when mixtures of these two soaps were present the emulsion was oil-in-water with an excess of sodium oleate and water-in-oil with an excess of magnesium oleate.

Exp. 106. A Four-layer Emulsion.—Leon W. Parsons finds that when a " Nujol " solution of magnesium oleate is shaken with an equal volume of water containing an approximately equivalent amount of sodium oleate, and

allowed to stand, a four-layer emulsion results. The top layer is "Nujol," and the bottom layer is water, but between these there is a double layer, the upper part of which is an emulsion (or cream) of water-in-oil, and the lower part a cream of oil-in-water These layers may be removed with a pipette and examined by the usual tests.

Glycerol and water are classed together as regards their insolubility in most other liquids; so by the phrase "water-in-oil" we may really mean "glycerol-in-oil." Cellulose nitrate is readily peptized by a number of liquids in which glycerol is insoluble, and hence aids in the formation of "water-in-oil."

Exp. 107.—To a 2 per cent solution of cellulose nitrate in amyl acetate, add glycerol in small portions with much shaking. An excellent creamy emulsion results The glycerol is dispersed in drops.

Make an emulsion of water-in-toluene by shaking water with a 2 per cent solution of raw crêpe rubber in toluene.

Exp. 108. How to Recognize Emulsion Types.—Heat powdered rosin in a heavy mineral oil until nearly 1 per cent has dissolved. Grind (or beat) water into this. Is it an emulsion of oil-in-water (the usual type) or water-in-oil?

Test this by attempting to dilute portions with water; with oil. Addition of the continuous phase gives ready mixing. Mixing does not occur if the dispersed phase is added in excess Or put a little emulsion on a glass plate and add one drop of either phase Whichever one spreads must be identical with the continuous phase.

A minute fragment of a fat-soluble dye, such as Sudan III or Scarlet R, gives a spreading color in an emulsion of water-in-oil but not in the other type Try all these tests on some of your emulsions. Oil-in-water is a better conductor of heat and electricity than water-in-oil Why?

Exp. 109. A Lubricating Grease.—To 100 cc. of some heavy petroleum fraction add 20 g of dry calcium oleate. Heat to 200° or higher, until the soap dissolves. Now cool with constant stirring, and as soon as the temperature falls below 100° add 5 cc of water, continuing the stirring until the mixture is cold An emulsion of water-in-oil is obtained, with a smooth, salve-like structure suited for cup lubrication.

Rape oil may be saponified with lime to furnish a good soap for the grease. Aluminum oleate is often used and a small amount of a sodium soap added to the other soap.

Transparent Emulsions.—Usually, when two transparent liquids are emulsified, a milky-white mixture results. Kerosene shaken with water gives such an emulsion; yet transparent emulsions can readily be prepared. Transparency depends upon the relative indices of refraction of the two liquid phases. If both phases have the same refractive index there will be neither

reflection nor refraction, and the system will appear homogeneous and entirely transparent.

Exp. 110.—Make a 2–4 per cent solution of dry calcium oleate in carbon tetrachloride (warming). Disperse glycerol in this by shaking. A good transparent emulsion is possible.

Shake a solution of 2 per cent raw crêpe rubber in " Nujol " with an equal volume of glycerol. What type is this?

Exp. 111.—Chromatic Emulsions (Holmes and Cameron, Jour. Am Chem. Soc. **44**, 71, 1922).—Shake 4 volumes of gycerol with 4 volumes of a 2-3 per cent "solution " of dry cellulose nitrate (11 per cent nitrogen) in amyl acetate. Add 10 volumes of benzene with shaking; then more glycerol, until rather viscous; then still more benzene in small additions, shaking, until color appears. The whole " chromatic," scale of colors may be secured by the addition of increasing amounts of benzene. The colors reappear in reverse order on the addition of more amyl acetate. Temperature changes change the colors. Such an emulsion is viewed best if a 125 cc. oil specimen bottle is used as a container and held some distance from the source of light. A single source is best, as one window in a room or a single strong light at night On long standing these emulsions " cream " downwards, although vigorous shaking restores much of their beauty The cream often sets to a real jelly

To secure such structural color emulsions it is necessary to have two mutually soluble liquids for the continuous phase, one of them of high refractive index and high dispersive power (as a prism disperses light). On careful addition of this liquid to a milky emulsion already prepared, it is possible to change gradually both the refractive index and the dispersive power This insures the chromatic range of colors Carbon disulfide may be used instead of benzene, rubber for the cellulose nitrate] and water solutions for the glycerol. Any constituent may be varied.

If carbon disulfide be used instead of benzene the emulsions are more beautiful and do not cream so soon A much smaller volume of carbon disulfide than of benzene is used in bringing out the colors

CHAPTER X

VISCOSITY

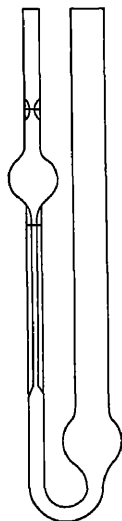
THE Ostwald viscometer is a suitable instrument for laboratory measurement of viscosities. It consists of a U-shaped tube with a small bulb emptying into a capillary for one arm and a much wider tube for the other arm. For ordinary viscosities the bulb should hold 2–3 cc. The capillary should have a diameter of about 0.5 mm. and a length of about 6 cm. The remaining sections of the tube in the capillary arm should have a diameter of about 4–5 mm.

Since viscosity changes with the temperature, the viscometer should be read in a thermostat. Of course absolute cleanliness of the capillary is essential. The tube should be treated with warm chromic acid solution, rinsed with water, alcohol and ether and dried with a current of warm air which has been freed from dust by passing through glass wool.

The liquid to be measured is pipetted into the larger arm and then carefully drawn above the bulb. As it falls (viscometer quite vertical) the stop watch is started as the liquid passes the upper mark and is stopped as it passes the lower mark.

FIG 16 —Ostwald viscometer

A simple 5 cc. pipette with a tip drawn out sufficiently small may be used for rough comparative work, and the time of outflow taken as a measure of viscosity. Even the time of fall of steel bicycle balls in viscous media may serve where only approximate results are wanted.

A very good commercial viscometer, now much used, is the improved MacMichael instrument. It operates on the principle of measuring by the angular torque of a standardized wire, the force

required to cause two surfaces, 1 cm. apart, to move past each other at the rate of 1 cm. per second, overcoming the internal friction of the liquid against itself throughout the space between the surfaces, a film of liquid moving with each surface and the layers of liquid between shearing past each other.

Bingham's new viscometer gives excellent results.

Viscosity of Gelatin.—Davis, Oakes and Browne (Jour. Am. Chem. Soc., **43**, 1526, 1921) show how the viscosity of gelatin "solutions" is influenced by age of the solution, concentration, temperature of preparation and character of the gelatin. They report a maximum viscosity at an age of twenty-four hours. Hydrolysis of gelatin by OH^- is quite marked. Bacterial decomposition has a strong influence. A good gelatin, after boiling a few minutes, is no better than a poor grade. It was their practice to bring all solutions to 75° for concordant results. Hydrolysis was usually slow at that temperature. Their directions for a measurement follow.

Exp 112.—Bring the gelatin and water (with acid or base if desired) to 75° in twenty minutes, stirring frequently Filter through glass wool and place in a thermostat at 25° Pipette 5 cc. into an Ostwald viscometer and immerse in the thermostat for ten minutes Draw the solution into the bulb of the viscometer and make the run while in the thermostat, timing the flow with the stop-watch The density is determined with a pycnometer The viscosity coefficient is calculated according to the customary formula

$$N \text{ (gelatin)} = N \text{ (water)} \times \frac{\text{Flow time in sec for gel.} \times \text{density gel solution}}{\text{Flow time in sec for water} \times \text{density water}}$$

N for water is taken as 0 008937 absolute unit.

Measure the viscosities of 0 5 per cent gelatin aged 5, 30, 60 and 120 minutes (or longer) and plot the curve.

Exp. 113. Viscosity Change of Benzopurpurin with Age.—Measure roughly with a pipette the time change in viscosity of a 0 4 per cent solution of benzopurpurin at 25°. Plot age of the solution in minutes against time of outflow in seconds

Exp. 114. Effect of Concentration upon the Viscosity of an Emulsion.—Using any convenient oil, prepare 5, 10, 20 and 30 per cent emulsions of oil in 3 per cent aqueous gum arabic. Plot viscosity against concentration of the oil. Note the similarity to solvated colloids in this respect

Exp. 115. Viscosity of Soap at Different Concentrations —With a pipette, make rough measurements at 20° of the viscosities of 0 05 N, 0 2 N, 0 4 N and 0 6 N solutions of potassium oleate (or sodium oleate) Plot time of flow in seconds against concentration This curve is typical of the solvated colloids.

Fischer's diagrams (" Soaps and Proteins," 70, 71), throw light on viscosity studies.

Hatschek states that if suspended particles do not rest on each other the viscosity-concentration " curve " is a straight line.

Wo. Ostwald believes that, other conditions being constant a dispersoid reaches its highest viscosity at a medium degree of dispersion. Jerome Alexander (Jour. Am. Chem. Soc., **43**, 434, 1921) enlarges upon this view with his discussion of the " zone of maximum colloidality." He states that clays hold increasing amounts of water as their particles become smaller. In that event the particles must act as liquids rather than as solids.

Bingham's work on " viscous and plastic flow " is published in book form by the McGraw-Hill Book Co. and is worth reading. He makes the interesting distinction that a viscous liquid will

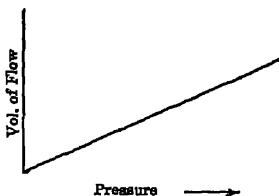



FIG 17 —Viscous flow

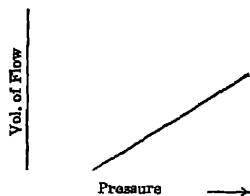



FIG. 18 —Plastic flow

start to flow, no matter how small a pressure is applied, while with plastic materials no flow takes place until after the pressure has exceeded a certain definite "yield value." Plastic substances he classifies as solids, and he insists that paints are not viscous liquids but highly mobile plastic solids. Even a very viscous substance, such as pitch, flows, under a very slight pressure, like water or any fluid.

Bingham states that the melting point of gelatin and other gels is the point where viscous flow changes to plastic flow. This suggests possible experiments with solvated colloids.

Bingham's elaborate but accurate viscometer and plastometer are now on the market.

The falling-sphere viscometer was used to measure the viscosity of cellulose nitrate solutions by Gibson and Jacobs (Jour. Chem. Soc. **117**, 472, 1920) and by Gibson, Spencer and McCall (Jour Chem Soc. **117**, 484, 1920).

CHAPTER XI

ADSORPTION FROM SOLUTION

It seems that every solid surface has an attraction for other substances, greater for some than for others. This holding to a surface we call adsorption, and we differentiate it from chemical reaction or solid solution. It may be due to free valence of the surface atoms; but, whatever it is, we are able to measure it and study it. Some solids have far greater adsorbing power than others, and a given adsorbent shows "preferential adsorption." Of course, the finer a solid is, the greater its surface area and the greater its adsorbing effect per gram Bone char is used to adsorb coloring matter from sugar solutions in refineries, fabrics adsorb dyes (in many instances), and most precipitates adsorb ions from solution. When glues adhere to a solid they must be powerfully adsorbed. "Adsorption may be considered a concentration of dissolved or dispersed substance upon the solid or liquid or gaseous adsorbing surface. After concentrating there the adsorbed substance may react or polymerize or dissolve or be coagulated or it may crystallize slowly."

Exp. 116. Adsorption of Glue.—Dissolve 10 g of dry glue in 30 cc of hot water. Pour it into a 100 cc beaker and set aside for a week or more to dry. As the glue contracts it pulls in the walls of the beaker, so powerfully does it adsorb the glass.

Exp. 117.—Filter night blue sol through a 15 cm. layer of precipitated and oven-dried silica. Use a tube 1 or 2 cm in diameter This suggests the use of sand filters in adsorbing bacteria from water.

Exp. 118.—Shake crystal violet (or other dyes), 2 mg to 100 cc of water, with 2 g. of powdered charcoal (blood charcoal is excellent) or fullers' earth. Is the solution colorless after settling? Pour off the liquid and add alcohol or acetone to the mud. What about the equilibrium concentration in the two cases?

Exp. 119. Spring's Soap Cleansing Experiment.—Wash animal carbon with alcohol and ether (to remove grease) Dry Rub the carbon on the *outside* of a folded filter, shaking off all loose material Rub also on the inside of another filter Pour water through each. Repeat with 1 per cent

soap solution (sodium oleate). Explain by the adsorption theory. Explain action of soap in cleansing the skin In the above experiment do not use a very dense filter paper. In cleansing the skin, soap may have to emulsify the grease or oil that glues dirt to the skin.

Read Hillyer's classic papers, Jour. Am. Chem. Soc., **25**, 511, 524, 1256 (1903).

Exp. 120. Adsorption by Barium Sulfate.—Add a neutral solution of sodium sulfate to a neutral solution of barium chloride After the precipitate of barium sulfate has settled, test the supernatant liquid with indicators.

Repeat the experiment, using potassium sulfate instead of sodium sulfate. Test the supernatant liquid with indicators. Explain the difference

Exp. 121. Adsorption by Barium Sulfate.[1]—Precipitate barium sulfate from a strongly alkaline solution of potassium permanganate. The precipitate remains rose-red, even after washing, boiling with hydrochloric acid (to remove manganese dioxide) and washing again. This adsorbed permanganate is too small in amount to measure quantitatively. It does not react with hydrogen peroxide, possibly because of great diminution of solubility or to the formation of some compound.

Exp. 122. Adsorption of the Base from Potassium Salts.—Shake a dilute solution of potassium chloride with cotton, with a soil; with carbon black. After it has been standing for some time, filter and test the filtrate with indicators. The solution is acid A potassium determination would prove that a loss of potassium had occurred.

Exp. 123. Adsorption by Humus.—Patten and Waggaman call our attention to a neat experimental demonstration of the adsorption of soluble material from solution, an experiment originally offered by Schumacher (Physik der Pflanze, 304, Berlin, 1867).

" Humus and a weak solution of oxalic acid were placed in a beaker. The humus adsorbed the oxalic acid from solution, and after the humus had settled and the supernatant solution had become clear, a little sack made of collodion, attached to a glass tube and filled with water and calcium carbonate, was suspended in the solution, not touching the layer of settled-out humus The oxalic acid of the solution diffused into the collodion sack and reacted with the calcium carbonate to form insoluble calcium oxalate. Thus the concentration of the oxalic acid solution is lowered and the oxalic acid adsorbed by the humus is practically all removed.

" This was shown by removing the humus and extracting with hot water. The filtrate showed no trace of oxalic acid The humus was free from bases, so that a chemical combination could not have been formed.

" If the humus had been in contact with a nutrient solution, and had adsorbed plant food from it, a plant whose roots were in the solution would have behaved in a similar manner, adsorbing the soluble matter from solution just as did the collodion sack containing calcium carbonate "

This experiment illustrates the reversibility of the adsorption process. Of course, in some cases this reversibility is affected by changes in the adsorbed material.

[1] Adapted from H. E. Wohlers, Zeit. anorg. Chemie, **59**, 203 (1908).

Exp. 124. Adsorption of an Indicator.—Shake finely powdered orthoclase (or other similar rock powder) with water to which has been added a very little phenolphthalein. A failure to develop pink color does not mean an absence of alkalinity Decant the clear solution after complete settling of the rock powder and add to the solution more phenolphthalein. A distinct pink color appears. Now add a little more rock powder to this pink solution and the color disappears.

Clarke showed the alkalinity of water in which rock powders have been in suspension (Bull. 167, U. S. Geol Survey, 156, 1900). Yet some powdered rocks in aqueous suspension show no red color with phenolphthalein. Of course, this is due to the adsorption of the color by the powder. Therefore, the test of alkalinity of a solution by phenolphthalein cannot properly be made if there are present in suspension finely divided particles which have the power of adsorbing the indicator.

Hulett and Duschak (Zeit. anorg. Chem., **40**, 196, 1904) have investigated the nature of barium sulfate precipitates, which are nearly always found to weigh too much, and attribute the results observed by them to the formation of a compound, $BaCl \cdot HSO_4$. On long standing or heating of the precipitate, hydrochloric acid was given off—which indicates that hydrochloric acid was adsorbed on the surface of the precipitate and escaped when the area of surface was reduced Barium sulfate has been found to adsorb many compounds from solution. Vanino and Hartl (Ber., **37**, 3620, 1904) observed that this precipitate adsorbs colloidal metals from solution. Patten (Jour. Am Chem. Soc., **25**, 186, 1903) found that barium sulfate adsorbs salts of nickel, cobalt, chromium, iron and manganese.

Exp. 125. Coarse and Fine Powders.—Fink (Jour. Phys. Chem, **21**, 32, 1917) and Briggs (ibid, **22**, 216, 1918) point out that fine powders adhere to coarser particles when mixed. A coarse red powder mixed with a very fine white powder looks white Also, a fine red powder mixed with a coarse white powder looks red. Obviously, this interests the man wishing to use cheap fillers in commercial products

Mix about 0.03 g of dry Prussian blue with 10 g of dolomite (or some convenient white powder) that passes a 40-mesh sieve but not a 100-mesh sieve What is the general color effect? Now mix the same weights, but use dolomite that passes a 200-mesh sieve Explain the difference Rouge or lampblack may be substituted for the Prussian blue

In a somewhat similar fashion, larger particles settling in a coarse suspension drag down the smaller particles with them.

Exp. 126. Adsorption of Alkaloids by Lloyd's Reagent.—Dissolve 1 g. of quinine bisulfate in 80 cc. of water and add 8.5 g of Lloyd's reagent (a hydrous aluminum silicate prepared from fullers' earth). Shake well and filter Test the filtrate for quinine by Mayer's test or any of the usual tests. Explain the result Now wash well with water, dry and extract the powder with fractions of 100 cc. ammoniacal chloroform Test the chloroform extract for quinine. Draw conclusions. We are indebted to John Uri Lloyd of Cincinnati for this experiment.

Exp. 127. Use of Fullers' Earth in Adsorption Filtration.—Fill two tubes, one containing fullers' earth previously heated to 300° and the other containing fullers' earth heated to red heat, with a heavy, dark, cylinder oil which has been warmed to 100° C, providing tubes with exit stopcocks or clamps. Allow to stand overnight; then run off effluent oil and note final color

Exp. 128. Water Rings and Capillary Spread.—Make a dilute solution of copper sulfate and cadmium sulfate Add ammonia until alkaline, and dilute until the blue color is scarcely visible. Let several drops fall on the center of a piece of filter paper and hold the paper over the mouth of a bottle of ammonium sulfide. Three rings appear—an outer water ring, a yellow ring of cadmium sulfide and a central black ring of mixed copper sulfide and cadmium sulfide.

The copper salt is most strongly adsorbed by the paper and hence diffused only a short distance, while the cadmium salt diffuses farther because it is less strongly adsorbed by the paper.

This method has been used for the analytical separation of copper and cadmium Bailey found that with increasing dilution the amount of separation became greater.

CAPILLARY RISE OF DYES

References: Pelet-Jolivet in Koll-Zeit, **5,** 238 (1909); Chem. Abs, **3,** 839 (1909); **4,** 829 (1910)

Exp. 129.—The capillary rise of dye solutions, on strips of linen, wool or silk, shows that capillarity is least when the dye is fixed directly by the material.

Dye bases rise less than dye acids. With methylene blue, addition of an acid increases the capillary rise of the dye and addition of a base decreases it. Try this and compare with ponceau

Does increased depth of immersion in the dye solution affect the rise? Try both methylene blue and crystal violet.

What is the influence of concentration on rise of color? Learn by experiment if capillary rise occurs when the dye is dissolved in acetone, alcohol or other non-aqueous solvents.

There is evidently a close relation between capillarity and the electric charge on particles.

Exp. 130.—Capillary rise of dyes in strips of filter paper increases as adsorption of the dye decreases Basic dyes are strongly adsorbed; therefore direct dyes show weak capillarity, increasing with the concentration of

the dye. Acid dyes exhibit strong capillarity, not increased by concentration.

Positive colloids are like the basic dyes in strong adsorption and weak capillarity. Try several. To one of these colloidal suspensions add less than enough hydrochloric acid to coagulate it, and note the change in rise. To a portion of the same suspension add sodium hydroxide, and measure the change in capillarity. (Molybdenum blue is a negative colloid while methylene blue is a positive colloid only in strongly alkaline solution

Exp. 131.—Sahlbom (Kolloidchem., Beihefte **2,** 79, 1910) followed the "membrane hydrolysis" of aqueous solutions of ferric chloride by noting the capillary rise of dialyzing solution after dialysis had continued for twenty-four hours, two days, three days, etc The molecularly dispersed ferric chloride rose high in a strip of filter paper; but as colloidal ferric hydroxide formed on prolonged dialysis, the rise of iron compounds decreased as shown by color. Such a positive colloid would, of course, be discharged and coagulated by the negative filter paper

Represent graphically this difference in capillary rise in the paper strips.

Exp. 132.—Hang strips of filter paper in colloidal ferric hydroxide and in colloidal Prussian blue. Explain the difference in rise. Remember that Prussian blue is a negative colloid and that the charge on paper in water is negative.

It has been urged by Wo. Ostwald that this capillary rise method should be used as a method of determining the sign of the electric charge on colloid particles. Thomas and Garard, in a paper well worth reading (Jour Am. Chem Soc., **40,** 101, 1918) take issue with Ostwald. They contend that the height of rise is wholly a matter of concentration, presence of electrolytes, the atmospheric conditions and the nature of the paper

H. B. Weiser states that electrolytes with anions that are not readily adsorbed precipitate the positively charged colloids in high concentration and the precipitates are readily reconverted to the colloidal state by washing on account of the ease with which the precipitating electrolytes are removed. Electrolytes with readily adsorbed anions precipitate in low concentration and this precipitation is irreversible since the strongly adsorbed anions are not readily removed by washing.

The Adsorption Isotherm.—Freundlich has stated that the quantitative adsorption of dissolved substances in relation to the end concentration can be expressed by the formula

$$x = a\ C^{\frac{1}{n}},$$

where x is the amount adsorbed by one gram of the adsorbing material, C is the end or equilibrium concentration in the liquid

after adsorption, and a and n are constants depending on the nature of the solution and adsorbent.

The value of $\frac{1}{n}$, Freundlich states, varies from 0.1 to 0.5, while a varies much more. The amount of adsorption by a given substance varies with the solvent, as shown by the fact that certain dyes powerfully adsorbed by glass from water solution may not be washed off completely by water, while alcohol quickly cleans the glass.

When we plot x against C, that is, adsorption against the equilibrium concentration, the curve becomes a parabola (or

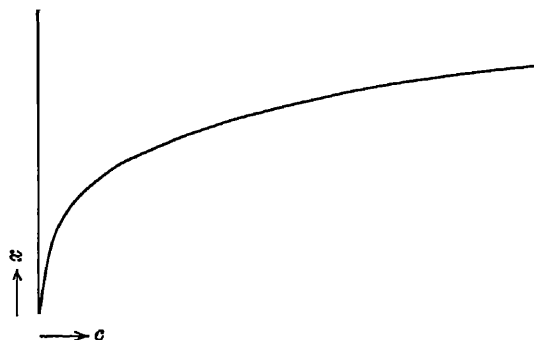



FIG. 19.—Adsorption isotherm

approximately so). The logarithm of the equation should plot as a straight line, but in practice it usually misses this ideal somewhat. In some instances the solvent is adsorbed as well as the solute, and this complicates matters. Adsorption is proportionally greater from very dilute solutions than from more concentrated solutions, which is certainly not true of reactions.

Exp. 133.—Freundlich (Zeit. phys. Chem., **57**, 385, 1906) states that if 1 g of charcoal or other adsorbent carbon be shaken twenty minutes by hand the system approaches the same equilibrium as that reached after twenty-one hours' shaking Quick surface adsorption is the main factor, not slow diffusion into the interior of particles.

Shake 1 g of blood carbon with 100 cc of 0 02 N acetic acid for six minutes (using a 300 cc Erlenmeyer flask) Let settle overnight and remove a convenient fraction with a pipette. Titrate with a standard base and record the acid concentration as C. Try similar experiments with a series of different concentrations, such as 0 03 N, 0.05 N, 0 01 N, 0 5 N, 1 N, 2 N, etc

Plot x against C. If the curve is nothing like a parabola, use more dilute or more concentrated solutions to extend the curve.

Since oxalic acid is adsorbed by charcoal and is easily titrated in very dilute solution by potassium permanganate, an experiment can be managed very well in much the same way as with acetic acid. The solutions of oxalic acid should vary from 0.1 per cent to 3 per cent, and extremely dilute potassium permanganate solution should be used in titration.

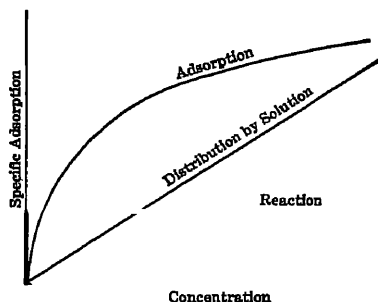



FIG 20.—Curves for adsorption, reaction and solid solution

Walker and Appleyard (Jour. Chem. Soc., **69**, 1336, 1896) outline a very good experiment on the adsorption of picric acid by silk. It is best to heat the silk in the bath only to 60°, as it becomes tender after a few hours at 100°.

In the same paper, Walker and Appleyard report an interesting experiment with picric acid and diphenylamine to show the difference between an adsorption curve and a reaction curve.

CHAPTER XII

ADSORPTION OF GASES

FIRST read the chapters on Adsorption in Bancroft's "Applied Colloid Chemistry."

The tenacity with which glass vessels retain a film of air when evacuated, even at elevated temperatures, shows us that a layer of gas molecules may be powerfully adsorbed by solid surfaces.

Fine powders "surge" when poured, and run almost like water if heated. Each solid particle is cushioned on a film of air. We have all noticed that phosphorus pentoxide "smoke" may pass through water, an astounding fact. In this case a strongly adsorbed film of air interferes with contact between the pentoxide and the water.

Carbon black, states Cabot, may occupy only 5 per cent of its own apparent volume, the rest being adsorbed air, and air free to move between particles.

Exp. 134.—Find the density of quartz (or any suitable solid) and then weigh 100 cc. of the same solid in finely powdered form Calculate the volume of air present in the 100 cc

To be exact, air is compressed by adsorption. Bancroft suggests a good experiment to demonstrate this.

Exp. 135.—Fill a 50 cc vessel with cocoanut charcoal and add water. Catch the air displaced by the water It may amount to 150–200 cc.

An excellent discussion of adsorption by cocoanut charcoal in gas masks is found in the report by Lamb, Chaney and Wilson, Jour. Ind. Eng. Chem , **11,** 420 (1919). They state that 1 cc. of war charcoal has a surface of 1000 square meters.

Langmuir's oriented adsorption theory is widely accepted. Particular groups in a compound may be strongly adsorbed by particular solid surfaces, thus placing the adsorbed molecules in a regularly arranged layer.

ADSORPTION BY SILICA GEL[1]

Exp. 136. Preparation of the Gel.—According to United States Patent 1,297,724 a highly adsorbent gel is secured after mixing (with constant stirring) hot solutions (50°) of hydrochloric acid containing 10 per cent of the gas by weight and an equal volume of sodium silicate of about 1.185 specific gravity This mixture sets to a gel in about one hour. The gel is broken into small pieces and washed free from acid and salt. Hot wash water hastens the process It is essential that the water be removed slowly in the drying operation The gel is first dried in a stream of air at 75° to 120°. The temperature is then slowly increased up to 300°

The final product is a hard, transparent substance resembling glass in appearance.

Properties of Silica Gel

Chemically, silica gel is a hydrated form of pure silica and is accordingly extremely resistant to most reagents. The material as shipped from the factory contains approximately 18 per cent water by weight. The water content is not fixed, since on exposure to air at ordinary temperatures, it will either take up or give off water, depending upon the water content of the gel and the humidity of the air.

Physically, it is a hard, semi-transparent glassy substance Its hardness on the mineral scale is about 5, and it undergoes but little abrasion with ordinary handling. It is capable of use either in powdered or granular form. The material as furnished to the trade does not undergo any volume change with variation in water content or when used to adsorb gases and vapors.

The paragraphs which follow are written with particular reference to the use of granular gel, the size of granules ranging from 8 to 14 mesh.

Activation

The gel, as furnished to customers, must be activated before use. This may be readily accomplished by heating to a moderate temperature in a stream of air for a few hours. For the activation of small quantities of gel (200 grams or less), a satisfactory procedure is as follows:

Exp. 137.—Place the gel in a tube not more than 1 5 inches in diameter, bent as shown in Fig. 1, immerse the tube in an oil bath at 150° C. and pass

[1] Adapted from bulletins issued by the Silica Gel Corporation of Baltimore

air, preferably preheated to the same temperature, through the gel at a rate of 25 cc. to 50 cc. per minute per gram of gel, for a period of two hours The gel should then be allowed to cool either in a stream of dry air or protected from atmospheric moisture by means of a drying tube This treatment will reduce the water content to 7 per cent or less and gives a product which is satisfactory for the adsorption at ordinary temperatures of vapors of liquids boiling between −10° C. and +150° C Activation should always be carried out in an air stream, the object being to carry away the water vapor given off by the gel and to assist in the distribution of heat.

The above procedure also applies to subsequent reactivations of the gel after use as a drying agent or after the gel has been exposed to steam, as in the recovery of solvents. The time necessary for these subsequent reactivations may be materially reduced, as experience dictates; but for the initial activation manufacturers of silica gel recommend two hours or more.

Prolonged heating at 600° C. will reduce the water content to 3 per cent or less. A small amount of water is essential to structure. An attempt to reduce the water content below 2 per cent generally results in a breakdown of structure, accompanied by a change in physical appearance. The clear, semi-transparent, glassy appearance is lost, and we have a milky-white, opaque substance left, which has but little adsorptive power. Whenever such white particles are observed after activation it indicates either that these particles have been subjected to too high a temperature or that the temperature was raised too rapidly at first. Patrick and Davidheiser recently prepared an active gel with a water content of only 0.33 per cent.

Activated gel should not be allowed to come in contact with water or other liquid and should not be exposed unnecessarily to a moist atmosphere.

Determination of Water Content

The water content of silica gel after activation may be readily determined by blasting a weighed sample of gel to constant weight in a platinum crucible.

Principles of Adsorption

In order to make clear the principles governing both adsorption and liberation of adsorbed material the curves shown in Fig 21 are reproduced here These are adsorption curves for sulfur dioxide, but will serve to illustrate general principles. They show,

at various temperatures, the relation between the quantity of sulfur dioxide adsorbed and the partial pressure or concentration of sulfur dioxide gas in the space surrounding the gel.

A statement of three general principles will help in the understanding of these curves:

1. The process of adsorption of a gas or vapor in silica gel is a reversible one.

2. Silica gel containing a definite amount of adsorbed gas or vapor at a given temperature will be in equilibrium with respect to a particular concentration of this gas or vapor in the space surrounding the gel.

3. The system made up of silica gel and gas (or vapor) having reached equilibrium at a particular temperature and concentration, this equilibrium will be disturbed by any change, either in temperature or in the concentration of the gas (or vapor) in the space surrounding the gel, and the gel will in consequence either liberate some of its adsorbed material or take up more. The accompanying curves indicate clearly the direction which such change will take.

If, for example, we pass over the gel at 100° C., a mixture of sulfur dioxide and air containing 4 per cent of the former by volume, adsorption will stop when the gel has taken up about 0.5 per cent of its weight of sulfur dioxide. After this amount has been adsorbed, the gas emerging from the gel chamber will have the same amount of sulfur dioxide as that entering the gel chamber. In other words, at 100° C., gel containing 0.5 per cent of its weight of adsorbed sulfur dioxide will be in equilibrium with respect to a mixture of this gas and air containing 4 per cent by volume of the former. If, however, we work at 40° C., the equilibrium point is reached only when the gel has adsorbed about 4.5 per cent of its own weight of sulfur dioxide. At 30° C. the equilibrium point is reached at 5 per cent adsorption, and at 0° C. at 14 per cent adsorption.

These curves also make clear to what extent the quantity of sulfur dioxide taken up by the gel is a function of the concentration of sulfur dioxide in the space surrounding the gel.

The effect of temperature is shown by the following: From a mixture of sulfur dioxide and air, containing 4 per cent by volume of sulfur dioxide (partial pressure about 30 mm.), the gel takes up 4 per cent, 6 per cent, 8.2 per cent and 11.1 per cent sulfur dioxide

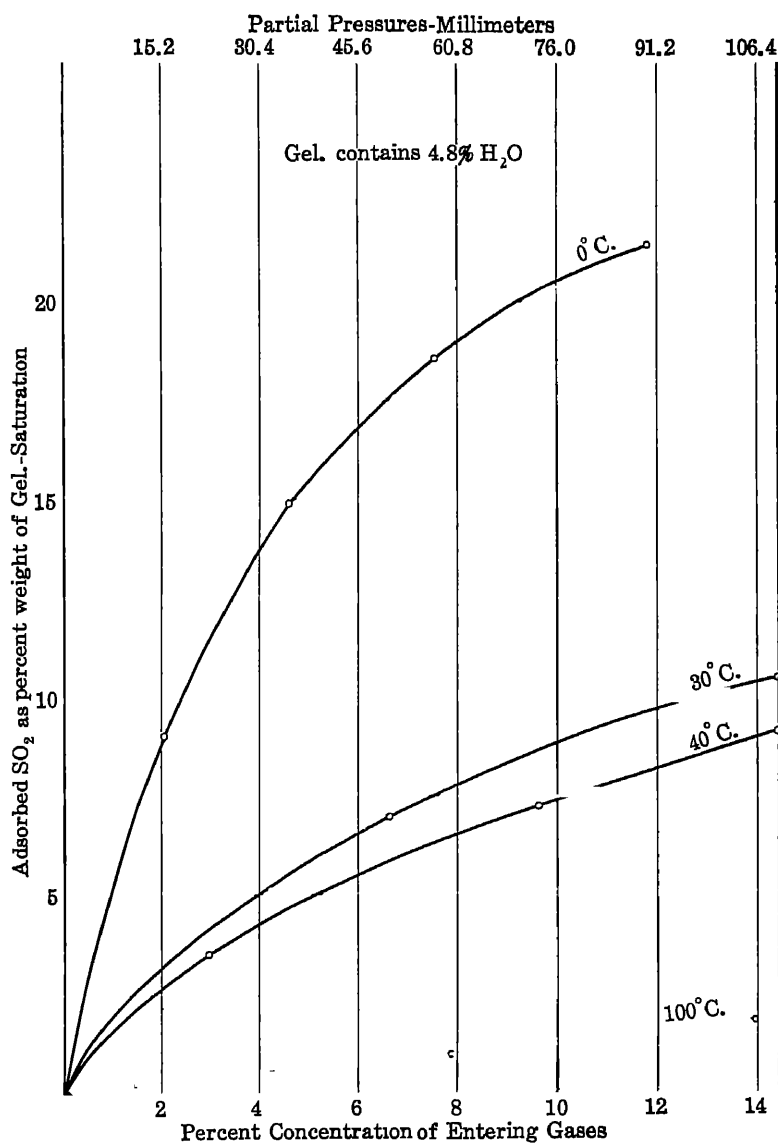



FIG 21 —Adsorption of SO_2

by weight at 40°, 30°, 20° and 10°, respectively. The effect of concentration may be illustrated by the following: At 30° the gel takes up 2.3 per cent, 6 per cent, 7.1 per cent and 8 per cent by weight of sulfur dioxide from mixtures containing 1 per cent, 4 per cent, 6 per cent and 8 per cent, respectively.

Since adsorption is a reversible process, it is clear that, having saturated the gel at a given temperature with respect to a particular concentration of sulfur dioxide, and keeping the temperature constant, if we reduce the concentration of gas in the space surrounding the gel the latter will give up its adsorbed material till a new condition of equilibrium is established with reference to the altered concentration. If at the same time we raise the temperature, the new equilibrium is reached more quickly and, at equilibrium, the gel will have less adsorbed material than at the lower temperature.

In practice, for the recovery of material which has been adsorbed in the gel at a comparatively low temperature, we do both; that is, we raise the temperature and reduce the partial pressure or concentration of the gas or vapor in the space surrounding the gel.

Working temperatures.—It will be clear from the curves that, for adsorption, the lower the temperature the better. In practice we generally adsorb at room temperature. For liberation of adsorbed material we work at temperatures ranging from 100° C. to 150° C., depending on the volatility of the substance in question. For the liberation of such liquids as ether, ethyl and methyl alcohols, benzene and water, 110° to 125° C. is ample. For high-boiling liquids, correspondingly high temperatures are required.

We may reduce the *concentration* of the gas or vapor in the space surrounding the gel in either of two ways:

1. By passing through the gel bed a stream of pure air, steam or other vapor.

2. By exhausting the vessel containing the gel.

By either of these methods we may bring about rapid liberation of adsorbed material at the temperatures given above.

It has been found that liquids of high boiling point are more strongly adsorbed than vapors from a liquid of low boiling point Furthermore, adsorption decreases with rise in temperature. Also, the greater the partial pressure of vapor being adsorbed, the

greater is the extent of the adsorption. All these facts suggest the idea of condensation of the vapor in the adsorbent.

All adsorbents are porous, with a large internal volume composed of exceedingly fine pores. Since a liquid in a small tube (capillary) possesses a lower vapor pressure than the normal vapor pressure, it must be easier to condense a vapor into a small capillary than on to a level surface.

Silica gel is used successfully at ordinary temperatures and under atmospheric pressure to remove from air the vapors of any liquid mixed with air in any proportions, provided the liquid boils, under atmospheric pressure, above $-10°$.

Apparatus and Method of Work

Adsorption

The apparatus required for a laboratory study of adsorption, by silica gel, of gases and vapors when mixed with air or other permanent gas consists essentially of the following:

1. Means of accurately measuring and controlling gas volumes passing through the apparatus train.
2. Means of mixing air and vapors in any desired proportions.
3. The adsorption apparatus proper.
4. Means of analysis of the gas mixture before and after it passes through the absorber.

For measuring the volumes of air or other non-corroding gas, we may use an ordinary gas meter. For accuracy, ease of control and convenience, the type of flowmeter and accessories employed by the Research Division of The Chemical Warfare Service is recommended. This apparatus has been fully described in a number of places, and a brief description of certain adaptations made by the Davison Chemical Company will suffice for our present purpose.

The essentials of an air flowmeter, with means of control and calibration, are illustrated in Fig. 22. Air enters at A under a pressure slightly greater than the head of water in F, and consequently a portion of it goes to waste through C. The balance, which is to be metered, passes through the stopcock K to the flowmeter, consisting essentially of a capillary tube D spanning the two ends of a U containing water or other liquid. The

pressure drop through the capillary is indicated by the difference in level of the liquid in the two arms of the U. The pressure in *G*, and consequently the pressure drop through *D*, is regulated by the stop cock *K*. The pressure on the left side of *K* should be slightly greater than the desired flowmeter differential. This pressure may be regulated by adjusting the head of water in *F* and, to a certain extent, by varying the volume of air going to waste through *C*. The head of water in *F* may be regulated by

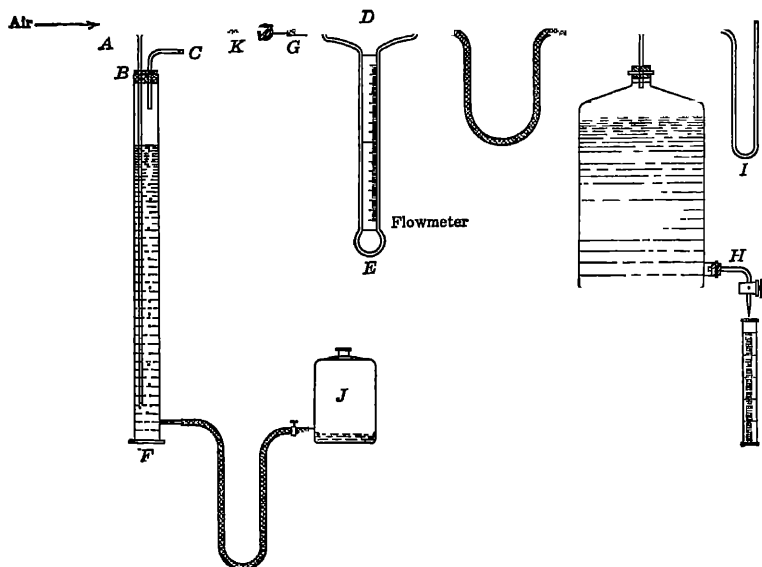



FIG 22 —Pressure regulator

raising or lowering the adjustable tube *B* or, more conveniently, by means of an adjustable reservoir *J*. The flowmeter differential should not be less than 10 cm. for the smallest volume of gas to be metered.

Fig. 22 also illustrates a convenient method of calibrating a flowmeter. The calibration consists in determining the relation between pressure drop and volume of gas passing through the flowmeter in unit time. If we maintain a constant pressure in *G*, as may be readily done by means of the arrangement shown, and draw off water at *H* at such a rate that the levels of liquid in the two limbs of the manometer *I* remain always the same, the air

will have passed through the flowmeter at a uniform rate and its total volume will be equal to the volume of water drawn off. In this way we ascertain the volume of air, in cubic centimeters per minute, which will pass through the flowmeter with the particular pressure differential employed, and we have one point on the calibration curve. By raising or lowering the adjustable tube *B* or the reservoir *J*, we can alter the pressure in *G* at will, and so determine as many points on the calibration curve as desired.

A flowmeter calibrated as above may be used as a standard in calibrating other flowmeters of approximately the same capacity.

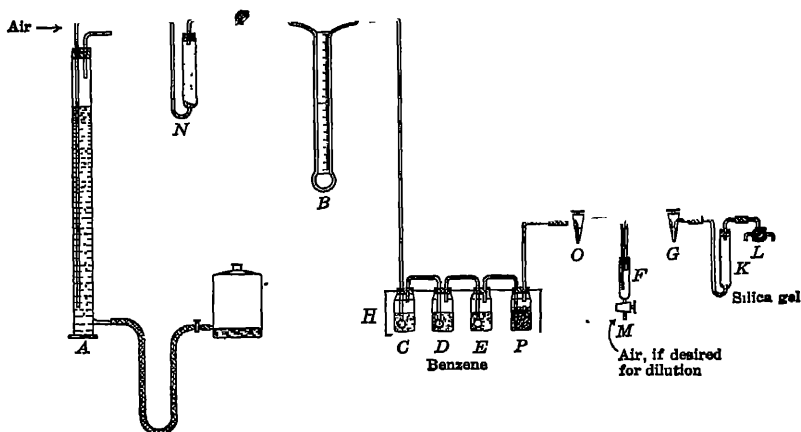



FIG 23 —Gas adsorption train.

The method described above is also applicable in calibrating flowmeters for gases other than air, provided a liquid is used in which the gas in question is only slightly soluble. For calibrating a flowmeter for small volumes (1 to 10 cc. per minute) of such a gas as sulfur dioxide, for example, analysis is preferable to the method described above.

The capacity of the flowmeter will, of course, depend on the size and length of the capillary *D* and the height of the U-tube *E*.

Fig. 23 gives the essential features of an apparatus for studying the adsorption of the vapor of a volatile liquid. A certain definite and constant volume of air per minute, dried at *N* and metered through *B*, is saturated at a desired temperature with vapor by being bubbled successively through at least three bottles,

C, *D* and *E*, containing the liquid whose vapor is to be adsorbed. The liquid in the saturators must, of course, be kept at a constant temperature by means of a properly regulated bath. A fourth bottle, *P*, should be loosely packed with glass wool to prevent liquid spray from being carried over. The mixture of air and vapor thus obtained passes into the mixer *F*, where it may or may not be diluted by mixing with a known volume of fresh air, metered separately and admitted at *M*. The gas mixture thus obtained passes from *F* to the absorber *K*. The three-way stopcocks, *O* and *L*, permit the taking of samples for analysis. The air admitted at *M* may be dried, or any desired amount of moisture may be introduced at this point. It is clear that by varying the temperature of the bath *H*, the relative volumes of air admitted through *B* and *M*, and the humidity of the air admitted at *M*, we can, in a very simple way, study adsorption in *K* under a wide variety of conditions.

This arrangement of the apparatus is intended for use when the air is saturated with vapor at a temperature below that of the room. If it is desired to saturate the air above room temperature, the mixer *F* should be placed in the same bath with the saturators *C*, *D* and *E*, and all connections submerged beneath the surface of the liquid in the bath.

For a study of the adsorption, by silica gel, of gases, instead of vapors of liquids, mixed with air, the air and the gas in question are metered separately in the desired proportions, mixed in a bottle or a vessel similar to *F* (Fig. 23) and are passed through the gel as before. Provision must, of course, be made for analysis of the mixture before and after it passes through the absorber.

Relation between Weight of Gel and Volume of Gas

The relation between the weight of gel in the absorber and the volume of gas passing per minute is, of course, subject to variation. We express this relation in terms of cubic centimeters per minute per gram of gel. Most of the work on which this discussion is based has been carried out with rates of gas flow ranging between 40 cc. and 100 cc. per minute per gram of gel. If granular gel is used, and the particles range in size from 8 to 14 mesh, a practical rate for adsorption in general is 50 cc. per minute per gram of gel.

This rate allows approximately 0.6 second as time of contact between gas and gel.

From what was said above, it is obvious that the procedure to follow in order to recover the adsorbed material consists in two steps: 1, raise the temperature; and 2, decrease the partial pressure of the vapor over the gel by evacuation or by displacement with air, steam or other vapor.

Thus, adsorbed water may be driven out by air at 115° C., more rapidly at 125° C., and still more rapidly at 150° C. High-boiling liquids may be adsorbed without difficulty, but require a correspondingly high temperature for recovery from the gel. Silica gel is almost ideally adapted to the adsorption and recovery of the vapors of liquids boiling between 30° C. and 150° C. in that it takes up large quantities of these vapors at room temperature and gives them up readily at slightly elevated temperatures, that is, from 100° C. to 200° C. This classification includes most of the important solvents, such as ether, acetone, methyl and ethyl alcohol, benzene, gasoline, methyl and ethyl acetates, and many others. It offers a satisfactory means for drying air and for the recovery and concentration of the vapors of more volatile liquids, such as sulfur dioxide.

Static and Dynamic Methods

The adsorption of sulfur dioxide by silica gel has been thoroughly studied by both the static and the dynamic methods.

The *static* method consists in placing a convenient amount of the gel in a small apparatus, which is then exhausted to the highest vacuum obtainable. To insure complete removal of air the vessel is heated to 300° C., and this temperature maintained, with the pump in continuous operation, for six hours, or until no more air can be pumped off. The pump used is the Gaede high-vacuum mercury pump. The vessel containing gel is then placed in a thermostat and a known amount of sulfur dioxide introduced. After the system has come to equilibrium, which requires not over fifteen minutes, the pressure is observed and the quantity of sulfur dioxide adsorbed is determined

The *dynamic* method consists in placing a convenient quantity of granular gel, usually 10 g., in a glass tube of 1 to 2 sq. cm. in section, bent in the form of a U for convenience of immersion in

the thermostat, and passing through the gel at a given temperature a definite mixture of sulfur dioxide and air. The air and sulfur dioxide are metered separately through carefully calibrated flow-meters similar to those used by the Chemical Warfare Service, passing first into a mixing chamber and thence over the gel. Under these conditions the gel adsorbs the sulfur dioxide completely for a certain period. At the end of this period a trace of gas begins to come through, the percentage of sulfur dioxide in the exit gas increasing rapidly, becoming finally equal to that of the entering gas. This corresponds to the point of saturation for this particular mixture and temperature.

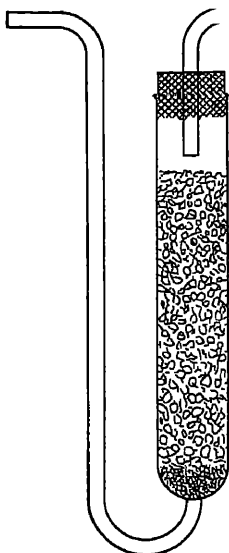



FIG. 24.—Tube of active silica gel.

A simple form of apparatus for carrying out this operation in the laboratory is shown in Fig. 5.

The gel tube *B* with its adsorbed material is immersed in bath *C*, and when the temperature of the gel reaches 100° C. steam is admitted at *A*. The mixed vapors are condensed in *D* and collected in receiver *E*. To minimize loss by evaporation through vent, etc., ice water should circulate through the condenser and the receiver should be surrounded by ice water. After displacement of the adsorbed material by steam, the gel, before being used again for adsorption, should be reactivated in an air steam as already described.

The method just described is in principle perfectly adapted to the recovery of liquids which, like ether, benzene, etc., are but slightly soluble in water, and do not react chemically with it. For substances which, like acetone and alcohol, are miscible with water, the distillate may require subsequent fractionation. For this class of liquids, recovery by evacuation instead of steam displacement may be preferable, from a practical standpoint Steam displacement may also prove impracticable for esters, such as ethyl and methyl acetates, on account of hydrolysis, with forma-

tion of acetic acid and alcohol. If for any reason steam displacement is impossible, the adsorbed material may be liberated by vacuum or by displacement with a vapor other than steam.

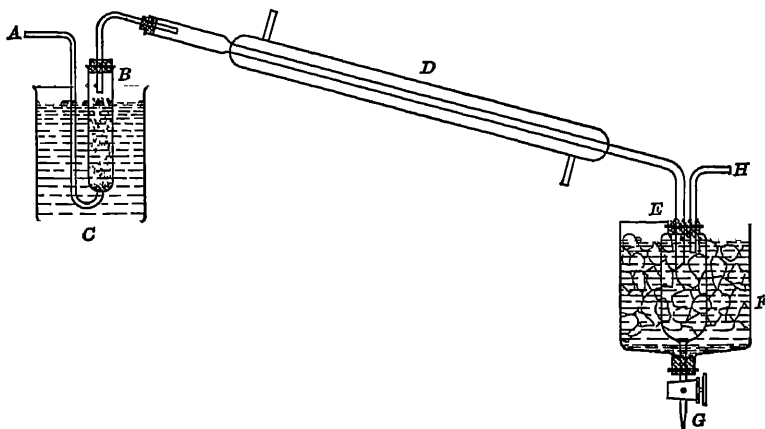



FIG. 25.—Recovery of adsorbed gases

Read a more detailed article on adsorption by McGavack and Patrick, Jour. Am. Chem. Soc., **42**, 946 (1920).

A series of experiments with silica gel, ferric oxide gel (as prepared by R. E. Wilson and Leon Parsons at Massachusetts

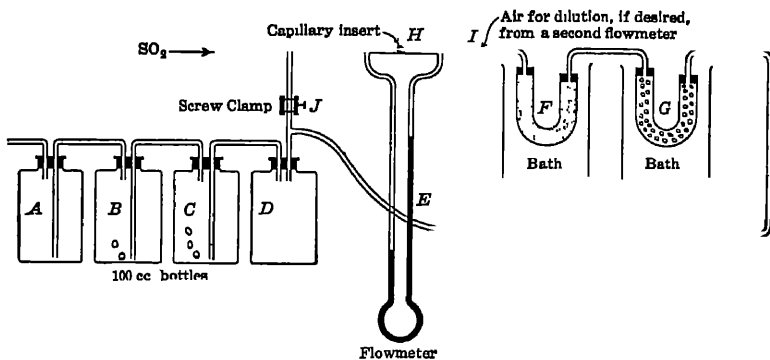



FIG 26 —Gas adsorption train

Institute of Technology) or similar gels may be performed with the apparatus described in Fig. 26. It is worth while to study the gain in weight of the gel at different temperatures, as well as at

different partial pressures of the gas adsorbed. Curves may then be plotted.

In Fig. 26 is represented an apparatus with which it is easy to determine when the active material is saturated (under the given conditions), or nearly so.

Sulfur dioxide is led through the train of 100 cc. bottles, *D*, *C*, *B* and *A* by opening and closing the proper screw clamps at *J*, etc. *D* is a safety trap; *C* is partly filled with water; and *B* and *A* contain a solution of sodium hydroxide to prevent sulfur dioxide from poisoning the air of the room. As soon as the water in *C* is saturated, the bubbles per second or minute are counted. Then the gas is shut off from this train of bottles and led through the flowmeter at *E*. It is warmed (if desired) by passing through the tube *F* filled with glass wool, and is adsorbed by the active gel in *G*

Fig. 27.—Capillary for flowmeter

Some unadsorbed gas passes on through the train of bottles, *D*, *C*, *B*, *A*. If the original rate of flow was 100 bubbles per unit of time and after passing over the adsorbent it is only 50 bubbles, it is evident that half the gas is being adsorbed. When no more is adsorbed the rate of bubbling rises to 100 again and the tube *G* may be weighed. A connection may be made at *I* with a second flowmeter from which air may be drawn for any desired dilution. A mixing bottle should then be placed at *I*. In this case the flowmeters are useful in showing the maintenance of flow of the gas. The capillary insert at H should have a fine opening barely large enough to be easily visible The best arrangement of the capillary insert is magnified in Fig. 27.

EXPERIMENTS ON FERRIC HYDROXIDE GEL

[Contributed by Dr. Leon W. Parsons of Massachusetts Institute of Technology]

Preparation of Ferric Hydroxide Gel

Exp. 138.—Mix 6 per cent solution of ferric chloride with 6 per cent solution of sodium hydroxide at 40° C. with vigorous agitation Allow the pre-

cipitated material to settle Wash repeatedly by decantation; finally on filter cloth Wash free of chloride. Dry the resultant material at about 110° C for several hours, finally in vacuo, if possible Screen to 8-14 mesh

This material is obtained in the form of a very active quasi-gel and may be used for various experiments on adsorption, catalysis, solvent recovery, etc., one of which is mentioned below.

Use of Ferric Hydroxide Gel for Solvent Recovery

Exp. 139.—Pass a stream of air through a test tube containing carbon tetrachloride and then through an ordinary U-tube containing iron gel (using two or three in series if necessary). Remove and weigh tubes at regular intervals, stopping experiment when tube No. 2 starts to gain weight The above experiment may be performed also with tubes containing charcoal, silica gel or fullers' earth The process of recovery of solvent may be illustrated by merely heating the materials, driving off the substances adsorbed.

EXPERIMENTS ON FULLERS' EARTH

[Contributed by Leon W Parsons of Massachusetts Institute of Technology]

Preparation of Fractions of Different Quality from Same Sample of Fullers' Earth

Exp. 140.—Heat a small portion of 15–30 mesh fullers' earth to the following temperatures, in a small iron crucible, cooling the resulting samples out of contact with air and stoppering the container tightly· 125° C, 300° C, 450° C, red heat. Use different samples for the following experiments. The earth heated to 450° and containing 3–5 per cent water is the most active.

Activity of Different Fractions of Fullers' Earth

Exp. 141.—Mix 10 cc of a solution containing 5 cc. pinene (157°–158°) and 5 cc xylol in a rough Dewar flask (made from two test tubes of different sizes) and add 2 5 g of each of the above samples of fullers' earth, stirring slowly with a thermometer and noticing the temperature rise with time. Xylol is merely a diluent. Try the experiment without xylol It is said that the earth acts catalytically to polymerize the pinene.

Behavior of Water of Constitution and Hygroscopic Water Contained in Fullers' Earth

Exp. 142.—Expose a small sample of fullers' earth, heated as above indicated to 450°, for one hour in a fairly humid atmosphere. Weigh out

2.5 g. and add to the above mixture of pinene and xylol, noting the temperature rise. Heat another 2.5 g. portion to 110° C. for a short period, noting the temperature rise on mixing with the pinene and xylol. Has the adsorption of a film of water made the earth more or less active?

Exp. 143.—Heat a sample of fullers' earth at about 300°–400° until it contains, say, 8 per cent of water. Now heat another sample much hotter until it contains decidedly less water. Then let it stand in moist air until its moisture content is also 8 per cent. Experiment will show that it is less active than the first sample. Why?

CHAPTER XIII

REACTIONS IN GELS

THIS chapter is largely composed of quotations from the author's own papers: Jour. Am. Chem. Soc., **40,** 1187 (1918); Jour Phys. Chem., **21,** 709 (1917); and Jour. Franklin Institute, **184,** 743 (1917).

The student should repeat a suitable number of the experiments, including at least those with gold, copper chromate and lead iodide.

As a preface to a study of crystal formation in gels, we must note their retardation of the rates of diffusion of acids, bases and salts, and their prohibition of diffusion of colloids. The mesh structure of gels must be practically equivalent to a network of capillary channels filled with the less concentrated phase. It follows, then, that the presence of substances affecting the distribution of water between the two phases must affect the size of these channels and change the rates of diffusion above mentioned. For example, Hatschek states that such salts as citrates and sulfates produce more rigid gels, but iodides and sulfocyanates retard or prevent gel formation Bechhold adds that sulfates, glucose, alcohol and glycerol retard diffusion, while urea, iodides and chlorides accelerate it.

The influence of certain gels—or jellies—on crystal growth is illustrated by many crystalline minerals It is probable that gelatinous silicic acid was the ancestor of vein quartz and by gradual dehydration became hard silica rock. In the gelatinous medium, reactions took place under conditions favoring the formation of crystalline veins For example, the reduction of gold salts produced crystals of gold, veining the gel, which later became quartz. A convincing part of this development can be reproduced in the laboratory

To the geologist, a working method of duplicating many such processes of nature must be of great value. To the chemist, a

study of reactions in gels gives a useful control of relative concentrations and velocity of reactions. The pathologist finds in the subject some relation to the formation of crystalline material in animal tissue.

METHODS OF WORK

The author found it convenient to mix equal volumes of solutions of sodium silicate and some acid, pouring the water glass into the acid and mixing quickly and thoroughly. Before the silicic acid set to a solid, one of the reacting salts was mixed with this solution, which was then poured into test tubes. After the gel set, the other salt solution designed to react with the first was poured on top. The solution on top should have a greater osmotic pressure than the gel, to insure reaction within the gel instead of above the surface.

The water glass used was a commercial grade known as "water white," with a density of 1.375. The ratio of the Na_2O to the SiO_2 was 1 to 3.5. When diluted to a density of 1.06 and titrated against hydrochloric acid, phenolphthalein being used as an indicator, it was equivalent to 0.51 N acid. With methyl red as indicator the normality was 0.57.

Pouring the mixture, before it solidifies, into the bend of a U-tube gives the experimenter excellent control of conditions. The two reacting solutions, poured separately into the arms of the U-tube, slowly diffuse through the gel and meet, often forming a sharp precipitation band. Any amount of either solution can be used in this method.

Hatschek, in some of his work, directs that the mixture of water glass and acid be dialyzed to free it from excess acid and salts. The addition of a very little ammonia sets the gel In other experiments he did not dialyze. The author does not find it necessary or desirable to dialyze out the acid and salts, as their influence on crystal formation or development of banding is beneficial in most instances. In a number of experiments he used a large excess of acid, and in others he added salts or non-electrolytes to secure certain effects.

Pringsheim states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film, if the solutions are isotonic. A hypertonic solution con-

tinues to diffuse into a hypotonic, and any precipitate formed is deposited in the latter. In accord with this idea, Hatschek often added indifferent substances to the solution on top of the gel in order to insure reaction below the gel surface.

Exp. 144. Lead Iodide.—Lead iodide crystals had been made by other investigators, but merited further study. This is one of the easiest to make, as well as the most spectacular, of all the crystal exhibits. A 1 06 water glass-N acetic acid mixture, containing 2 cc of N lead acetate to every 25 cc. was poured into test tubes After the silicic acid gel set firmly, it was covered with 2 N potassium iodide A compact layer of lead iodide quickly formed on the surface, followed very soon by crystallization below the surface of the gel. In a few days fern-like fronds grew down into the gel, mixed with many hexagonal plates. These concentrations may be varied with interesting results, and the lead salt may be used above the gel with the potassium iodide in the gel. The first order is much better. Magnificent golden fern fronds, 8 cm in length, and nearly perfect hexagons, 5 mm in diameter, were obtained in some experiments In one or two tubes, six hexagons grouped around a center, their arrangement greatly resembling that of some snow crystals. On standing in direct sunlight for several months, the lead iodide crystals blacken somewhat.

Exp. 145. Copper.—Perfect tetrahedrons of metallic copper were obtained in a 1 06 water glass-N acetic acid made 0 05 N with respect to copper sulfate. The gel was covered with a 1 per cent solution of hydroxylamine hydrochloride In a week or two the tetrahedrons were large enough to be observed with the unaided eye. Those formed near the surface were much smaller than those at greater depths Of course, the farther the reducing solution diffused into the gel the more dilute it became In a beam of sunlight the faces of the tetrahedrons gleamed with a splendid copper luster In nearly all experiments one or more groups of overlapping tetrahedrons were noted These formed in three radiating lines, making angles of 120°, or in some instances of 60°, 120° and 180°. This arrangement of copper crystals is found in mineral deposits All the other reducing solutions tried were inferior to hydroxylamine.

Exp. 146. "Lead Tree."—Simon grew the well-known "lead tree" in a silicic acid gel containing lead acetate A bit of zinc or tin was pressed into the top of the gel The author found that if the gel is about 0.02 N with respect to lead acetate a splendidly branching tree grows and may be handled roughly since it is supported on all sides by a solid.

Theory.—To prove that a gel was not necessary to account for crystal formation by regulated diffusion, the author filled the bend of a U-tube with alundum powder In one arm of the tube he poured a solution of potassium dichromate and in the other a solution of silver nitrate. Slow diffusion through the capillary spaces of the alundum allowed the formation of crystals of silver

dichromate, 1 cm. in length. Similar experiments, although not so striking, were performed with barium sulfate powder, flowers of sulfur and closely packed asbestos. In repeating such experiments the difference in concentration of the solutions in the two arms of the U-tube should be varied throughout a series.

Without doubt, any compact mass of insoluble discrete particles with proper-sized capillaries will function as a gel in favoring the formation of crystals. Other influences may be present in a true gel. Adsorption, pressure and solubility effects may greatly influence the capillary space results. A rather amorphous insoluble compound, first formed by the meeting of two reacting substances in a relatively narrow channel, may further regulate the rates of diffusion in such a way as to give time for crystal formation of more of the same insoluble compound. In this suggestion the geologist may possibly find an explanation of the marked crystalline nature of some mineral veins. The pathologist, too, may obtain some light on the accumulation of crystalline deposits in animal tissue

Exp. 147. Crystals without a Gel.—To test the theory, the mouth of a 10 cc. specimen tube was covered with a sheet of gold-beater's skin, held on firmly with a rubber band. The tube had first been filled with a solution of 0 1 N potassium iodide. Care was taken to leave no air bubbles on the under side of the membrane and to rinse the outside of the tube. The tube was then immersed in a small beaker of saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane, and in less than a minute crystals of lead iodide fell in a beautiful gleaming shower, rapidly increasing in amount. It is very easy to secure gleaming crystals of lead iodide by cooling its hot solution, but in this experiment the solutions were cold. If the same solutions are mixed in a test tube without the use of a membrane, a yellow powder results

When the more concentrated solution was placed inside the specimen tube, the crystals formed on the upper surface of the membrane This is in accord with the osmotic difference rule of Pringsheim. With less difference in concentration of the reacting substances in the solutions, the reaction was much slower

Separating solutions of silver nitrate and potassium dichromate in this way, it was a simple matter to make a gram or two of brilliant crystals of silver dichromate which settled to the bottom of the tube. Possibly this method may be of some use in the preparation of pure compounds, since the crystals are not mixed with an annoying gel. Other thin, semi-permeable membranes

serve. Parchment paper is good, but gold-beater's skin is most suitable.

To carry the theory further, the only need of the gold-beater's skin is to prevent sudden wholesale mixing of the solutions and mechanically sustain the rather amorphous precipitate first formed, which then functions as the real active membrane This theory is not universal in its application, for in gels excellent crystals of a number of substances formed without the appearance of a preliminary compact layer of precipitate In these instances only the gel functions in regulating diffusion The theory does apply, however, in the absence of a gel and in all instances where a compact precipitation band is formed

RHYTHMIC BANDING

Rhythmic banding of precipitates was first observed and recorded by Liesegang, hence the name " Liesegang's rings." His original experiment dealt with the rhythmic precipitation of silver chromate in gelatin. A solution of silver nitrate was poured on a solid gel containing dilute potassium chromate. The precipitate of silver chromate formed was not continuous but marked by gaps or empty spaces at regular intervals.

Exp. 148. Liesegang's Rings.–Prepare a gelatine gel containing 4 g. of gelatin, 0.12 g of potassium dichromate and 120 cc of water Let it cool in the ice-box. When it is firm, carefully remove from the beaker and immerse in a solution of 8 5 g. silver nitrate in 100 cc of water The gel must be completely covered with solution Replace in the ice-box for a day or two and then pour off the silver nitrate; rinse and cut a slice through the middle of the gel. Remarkable bands of silver dichromate are seen This experiment is from Liesegang and Wo Ostwald

Exp. 149. Mercuric Iodide.—A tube of silicic acid gel (from mixing equal volumes of 1 06 density water glass and N acetic acid) was made 0 1 N with respect to potassium iodide and covered with 0 5 N mercuric chloride In a few days, bands of red crystalline mercuric iodide began to appear These bands were not sharply marked for the first cm or two below the surface of the gel, but below that depth were excellent. In some tubes there were 40 bands, rather sharply marked, in a distance of 8 cm The spaces between the thin disks contained many scattered crystals

In a U-tube with a gel filling the bend, 0.5 N mercuric chloride in one arm and 0 1 N potassium iodide in the other, the sharp red bands of mercuric iodide followed the curve like ranks of soldiers pivoting in regular formation The excess of mercuric chloride diffusing into the gel reacted with the red mercuric iodide, forming a soluble colorless double salt, leaving

the gel somewhat clearer where the red bands had been. This gave the appearance of shadow bands following in the rear.

The presence of glucose in the gel made the bands very much sharper. Sodium chloride, on the other hand, diminished the tendency to band and in sufficient concentration prevented it altogether. In a gel of the composition described above but containing an added 10 per cent of sodium chloride, the mercuric iodide formed, not in the usual red needles, but in much larger crystalline aggregates, and very few bands appeared The crystals were scattered in an irregular way The addition of sodium chloride to the amount of 25 per cent of the weight of the gel caused the appearance of still larger widely scattered crystalline aggregates. Neither needles nor bands were in evidence. Since a gel made from sodium silicate and hydrochloric acid contains considerable soluble chloride, no sharp banding of mercuric chloride could be expected under such conditions. This may explain why earlier investigators in this field failed to record the beautiful examples of banding possible with mercuric iodide It is worthy of note that when mercuric nitrate was substituted for mercuric chloride still finer banding was obtained This may be due to the absence of chlorides or in part to the fact that mercuric chloride is less ionized than mercuric nitrate

FIG 28 —Rhythmic bands of mercuric iodide in a silicic acid gel

Exp. 150. Copper Chromate.—The banding of copper chromate in a silicic acid gel of very slightly basic reaction affords the best material for a detailed study of the phenomenon Gold banding is often more beautiful, but the remarkable sharpness of the layers of copper chromate and the perfect clearness of the gaps excel all other examples.

A gel from mixing equal volumes of 1.06 density water glass and 0.5 N acetic acid was made 0 1 N with respect to potassium chromate (before solidifying) and was later covered with 0 5 N copper sulfate In a day or two, bands of apparently amorphous copper chromate formed The first layer was often rather deep, 1 cm or more, then a clear gap with no trace of a precipitate of copper chromate, below that a much thinner band, more gaps and bands, the gaps widening steadily.

These relative distances varied not only with the initial concentrations of the reacting solutions, but also with the volumes of the potassium chromate solution in the gel and the copper sulfate

solution above. It is, of course, apparent that these relative volumes greatly influenced the rates of decrease in the initial concentrations. The distances were also influenced by the substitution of other acids for acetic in making the gel. The first deep band at the top always showed more or less distinct marks of smaller bands merging rather hazily into one. In reality, then, the bands steadily increased in thickness from the first as did the width of the gaps.

Fig. 29 —Copper chromate bands in a slightly basic silicic acid gel.

In a typical gel made as above, the depth of the first solid band or group of bands was 8 mm., the first definite gap 2 5 mm., the second band 2.5 mm, the next gap 7.5 mm., the next band 2 mm., the next gap 15 mm. and the next band 7 mm. In general, the best results were obtained by using 0 5 N copper sulfate and 0.1 N potassium chromate. With a saturated solution of copper sulfate there was no banding, merely a vague precipitation zone of copper chromate. But even this applied only to the ordinary test tube used. In a very long column of gel covered with a relatively small amount of saturated copper sulfate solution, the copper salt solution must become more dilute, as it diffuses to greater depths and finally reaches a suitable concentration for sharp banding

Making the gels by substituting 0 5 N hydrochloric or sulfuric or nitric acid for the 0.5 N acetic acid described above produced a striking change in the banding The gaps were more nearly equal and none of greater depth than 3 mm. With bands, many of which were 4 or 5 mm. in thickness, an ordinary test tube contained as many as 28 in a distance of 8 cm. The results with these 3 types of gels differed very little, except that the gaps in the sulfuric acid gel were not clear.

Working with acetic acid as in the first experiments discussed, the effect of increased alkalinity was studied. In a gel made from equal volumes of 1.09 density water glass (as compared with the usual 1.06 density) and 0.5 N acetic acid, the copper chromate bands were much closer together, greatly resembling an agate. Thirty in a distance of 3 cm. were obtained. With a gel from 1.15 density water glass and 0.5 N acetic acid the bands were still more compact. It is evident that an increase in the excess of sodium silicate, with its resulting alkalinity, brings the bands of copper chromate closer together.

Addition of sugar to the usual gels made the bands thinner. Urea had the opposite effect. The influence of gravity was shown by corking tubes and inverting. The bands were irregular and made up of crescent-shaped fragments. It is noteworthy that the final condition of many tubes showed the blue of the copper sulfate in all the clear gaps—even below the last band.

Exp. 151. Gold.—To 25 cc of a mixture of equal volumes of 1.16 density water glass and 3 N sulfuric acid was added 1 cc. of 1 per cent gold chloride. The solid gel formed in a day or two and was then covered with a saturated solution of oxalic acid (about 8 per cent). As the oxalic acid diffused into the gel the gold chloride was reduced A wonderfully beautiful series of colored bands of colloidal gold developed, with sparkling golden crystals scattered throughout the gel The upper layer of the first bands was red, the next blue and the next green A comparatively clear gap below this series was followed by another red-blue-green zone Usually after the first few rainbows the red was omitted A dozen or more such complex bands in an ordinary test tube were not uncommon, the upper bands measuring about 1 cm. in depth.

These concentrations of the gold chloride and the oxalic acid were varied somewhat, with no improvement in results. However, when the gel was made from 1.06 density water glass and 3 N sulfuric acid (setting in about one week) no bands of colored colloidal gold appeared—or only traces of them—but great numbers of gleaming yellow crystals of gold formed throughout the gel—strikingly beautiful in a beam of sunlight

These bands have been obtained before, but the author found the use of sulfuric acid in making the gel a very great improvement. When hydrochloric acid was used the colored bands were quite inferior. With acetic acid instead of sulfuric, no bands appeared, but the gel was colored uniformly with violet-blue colloidal gold. However, loading an acetic acid gel with consider-

able sodium sulfate developed a few shadowy bands. Evidently the influence of sulfates was a factor of importance.

Exp. 152. Basic Mercuric Chloride.—The author poured a basic gel, 1.08 water-glass-0 5 N acetic into a test tube and, with no other added salt, covered the gel with saturated mercuric chloride solution. Shining red-brown leaves appeared. Since they could not be obtained in a gel of acid reaction nor with any salt other than mercuric chloride, they were evidently one of the basic mercuric chlorides. A search of the literature justified this theory. Different basic chlorides are on record, but the description of $HgCl_2 \cdot 2HgO$ agrees perfectly with the crystals obtained above.

Gels of different basicity were covered with mercuric chloride solution and the crystals compared With 1 06 water-glass-0.5 N acetic (very slightly basic) the crystals were more widely scattered and, at a distance of a few centimeters from the surface of the gel, were excellent. This particular gel caused the most remarkable banding of the basic chloride With a very basic gel the crystals were smaller and formed in a rather compact mass. A few grams of glucose in 25 cc of a slightly basic gel changed the results decidedly. Instead of the brown-red leaves, a gray mass of closely packed bands, sharply marked, appeared. In a distance of 8 cm over one hundred of these bands were counted.

Theory

The experimental evidence given above justifies the advancement of a more detailed theory of rhythmic banding. For the clearest illustration, consider the copper chromate banding.

The gel (a silicic acid gel of slightly basic reaction) contains a dilute solution of a chromate and, above it in the tube, a solution of a copper salt. The copper ions diffuse into the gel, meet the chromate ions and form a layer of insoluble copper chromate at the surface of the gel. The chromate ions immediately below this precipitation zone diffuse into this region, now depleted of chromate ions, and meet the advancing copper ions, thus thickening the layer of copper chromate. According to Fick's law of diffusion, the rate of diffusion is greatest where the difference in concentration of the chromate ions in two contiguous layers is greatest, that is, just below the front of this thickening band of copper chromate. As a result, the region near the band decreases in concentration of the chromate ions faster than does the space below. Finally the copper ions have to advance some distance beyond the band to find such a concentration of chromate ions that the solubility product of copper chromate may be exceeded and a new

band formed. This repeats again and again. Of course, if the copper ions were retarded sufficiently there would be time for the concentration of the chromate ions again to become uniform throughout the remaining clear gel, and no gap would occur. Hence, if the diffusion of the copper ions is retarded by any means, the clear gaps decrease in depth—the bands are closer together. If copper ferrocyanide bands are formed in a similar manner they almost merge after the first layer reaches a thickness of a few centimeters. Yet they are distinct and agate-like. A precipitate of copper ferrocyanide greatly retards the diffusion of the ions that form it; hence we have here the proper condition to reduce the clear gaps to a minimum depth.

Fig. 30.—The influence of chlorides on the distribution of mercuric iodide. The tube on the left contains sodium chloride—the others do not

The permeability of the gel, as influenced by the presence of various salts, and sugars, for example, was found to be an important factor in rhythmic banding. With mercuric iodide in a silicic acid gel, the presence of sufficient sodium chloride entirely prevented the arrangement of the crystals in bands. On the other hand, glucose in a similar gel greatly favored the banding of mercuric iodide. In another experiment glucose produced a great increase in the number of bands of basic mercuric chloride. This marked influence of some salts gives importance to the selection of the acid used in making the gel. Hydrochloric acid is a poor choice when experimenting with mercuric iodide banding.

CHAPTER XIV

EXPERIMENTS WITH THE ULTRAMICROSCOPE [1]

THESE experiments are adapted to the dark-field illuminators of Bausch and Lomb, Leitz and Zeiss. The makers give full instructions regarding centering, adjustment, illumination, etc. Knowledge of microscopic technique is assumed.

Exp. 153. Ordinary Brownian Motion vs. Zsigmondy-Brownian, or Ultramicroscopic, Motion.—First observe the ordinary Brownian motion (in a dilute suspension of clay, kaolin, pollen dust, etc) of particles at the limit of visibility in a compound microscope with a 1/12 oil immersion objective. This motion consists in an uneasy *oscillation about a mean position.*

Then adjust the dark-field attachment, and observe a slide made with a dilute solution of benzopurpurin (1 drop of a saturated solution to 50 cc of distilled water), or a dilute solution of milk (about 5 drops of fat-free or bottom milk to 50 cc. of distilled water). Be sure to focus on the layer of fluid *between* the slide and the cover glass, for the glass surfaces themselves usually show motionless ultramicrons, illuminated scratches, etc. Dilute sufficiently to secure a field wherein individual ultramicrons may be distinguished. The ultramicroscopic particles show violent *free-path motion,* and move all over the field, passing in and out of focus What we really see are diffraction images, the particles themselves being smaller than a wave-length of light Large particles of incidental impurities (like fat globules in milk) reflect so much light that they render most ultramicrons invisible, just as the full moon renders most stars invisible. Note that the " Brownian " movement of fat globules (especially small ones) seems to be due to the blows they receive on all sides from colloidal particles, which in turn may owe their motion largely to the blows of the invisible crystalloid particles.

Exp. 154. Crystalloidal vs. Colloidal Solution.—Prepare a slide with alcoholic solution of potassium oleate (tincture of green soap) and observe that, outside of casual impurities, it shows no visible particles. Then, watching all the while, allow a droplet of water to diffuse between the slide and the cover glass The soap will practically explode into the colloidal state, and after the violent diffusion streams quiet down, the field will be full of ultramicrons in rapid motion.

Exp. 155. Precipitation and Protection.—Allow a droplet of dilute acid (HCl or vinegar) to diffuse under the cover glass of a slide of dilute milk or

[1] Contributed by Jerome Alexander, of the Uniform Adhesive Co

benzopurpurin solution prepared as in Exp. 1. After the diffusion currents cease, watch the gradual aggregation of ultramicrons At first they form groups of two or three. As the groups increase in size their motion diminishes, until finally there are large motionless or slowly floating grape-like clusters or masses. By using very dilute solutions and weak acid, the time of coagulation may be extended to half an hour or more.

Now add some warm gelatin or gum arabic solution to the dilute milk or benzopurpurin, and observe that the coagulating action of the acid may be partially or entirely prevented, most or all of the ultramicrons maintaining their isolated active motion

Note also by test-tube experiment that the addition of HCl to benzopurpurin solution produces a color change from red to blue, accompanied by precipitation. (The dye is a "soluble" sodium salt, and the precipitate the "insoluble" color base) If a protective colloid (gelatin or gum arabic) be added to the benzopurpurin solution prior to the addition of the acid, the color remains red or reddish-brown even though enough acid is added to produce marked turbidity. Compare the macroscopic with the ultramicroscopic findings. (See Jour. Soc Chem. Ind, **30,** 517, 1911.)

Exp. 156. Enzyme Action.—Observe the action of diastase on starch, and of pepsin on partially coagulated dilute egg-albumen solution. (See Jour Am Chem Soc., **32,** 682, 1910)

Exp. 157. Mutual Coagulation.—Observe the mutual coagulation of colloidal gold and colloidal As_2S_3. (Diphtheria toxin is "precipitated" by diphtheria antitoxin, but not by tetanus antitoxin, which, however, coagulates tetanus toxin. These reactions may be followed ultramicroscopically, but it should be remembered that the toxins are highly poisonous, the smallest trace in a scratch may produce serious if not fatal consequences)

Exp. 158. Blood.—Examine fresh blood, observing colloidal "blood dust" and red blood corpuscles for comparative motion. Watch fibrin formation or coagulation.

NOTE.—Read King's short article on Ultramicroscopy, pages 31–41 of the "Third Report on Colloid Chemistry," published in 1920 by the British Association; also pages 122–127 in Bechhold's "Colloids in Biology and Medicine."

CHAPTER XV

SOILS AND CLAYS

THE productivity of a soil is closely related to its colloid content. Weathering of feldspar yields much colloidal material in the form of alumina and silicic acid. This, with colloidal hydrated oxides of iron and humus, gives soil the proper physical condition.

Permeability, capillarity, adsorption and moisture content depend more upon the physical state of a soil than upon its chemical condition. J. M. van Bemmelen (Die Absorption, Dresden, 1910) states that the ability of soils to take up salts of alkaline earths and alkalies from solution is due to the content of basic silicates, soluble in hydrochloric acid, which act by an exchange of bases.

Humus is an indefinite mixture of organic substances, the debris of bacteria, plants and animals Manure, plowed-under crops and sods increase the humus content This humus acts as a protective colloid tending to keep much of the soil in the hydrosol state. It is opposed by the coagulating tendency of an excess of salts, by heat with drying and evaporation, and by freezing.

Soils have been ruined by a flood of sea water and by an overdose of fertilizing salts. On the other hand, Cameron and his assistants found that a certain non-productive soil was improved by treatment with tannin. This is a reminder of "Egyptianized clay" and of Acheson's graphite in which tannin acted as a dispersing or peptizing agent.

The ceramic chemist calls a clay weak, lean or sandy and lacking in plasticity if it has too little colloidal material. If it has too much he calls it fat, strong and sticky. A moderate plasticity is desirable for his purposes. Highly colloidal clays shrink too much on drying and firing

It has been found that clays may be given the fluidity needed for proper pouring into molds by the peptizing action of hydroxyl

ions from a little sodium carbonate. Then, on drying, there is less water to evaporate and consequently less shrinkage

Cushman (Jour. Am. Chem. Soc., **25**, 451, 1903) shows that the cementing power of rock powders is due to the formation of gelatinous silica, ferric oxide, etc.

Many soils adsorb the base from blue litmus more readily than the acid and give a false impression (due to the reddening of the blue paper in contact with soil) that a free acid was present in the soil. Cameron showed that moist cotton in contact with blue litmus does the same thing.

Exp. 159. (1) Determining the Amount of Colloidal Matter in Clays.— Moore, Fry and Middleton (Jour Ind Eng Chem., **13**, 527, 1921) separated the colloidal material from clay by the use of a Sharples centrifuge (17,500 times the force of gravity). This "ultra clay" consists mainly of hydrated aluminum silicate mixed with ferric hydroxide, silicic acid, organic matter and possibly aluminum hydroxide. Suspended in water, it exhibits good Brownian movement As a binding material it is much stronger than Portland cement, when dry.

Their method of determining the adsorptive power of ultra clay towards ammonia may well be applied to studies of other solid materials and other gases.

"Ultra clay was dried in an oven at 110° C for twenty-four hours. It was immediately transferred, while still hot, to a Schwartz U-tube, and weighed, and the tube was placed in a train of drying apparatus The Schwartz tube was then immersed in boiling water and thoroughly evacuated with an oil pump. The U-tube was next placed in an ice bath, and dry ammonia gas was passed over the ultra clay until it would adsorb no more under a pressure of one atmosphere The current of gas was then shut off and the apparatus allowed to stand for one hour to make sure that equilibrium had been reached as shown by a manometer attached to a U-tube The next step was to draw off the ammonia and collect it in a train of absorption apparatus filled with a saturated boric acid solution. When a good deal of ammonia had been drawn off, the U-tube was again placed in boiling water and the residual ammonia displaced with a current of air. The ammonium borate solution was titrated with 0.1/N sulfuric acid, using methyl orange as indicator "

The adsorptive power of soils towards gases is undoubtedly due largely to their colloid content ("ultra clay"). The authors quoted above destroyed the colloidal condition of a certain clay by heating to 1130° C and then measured its gas-adsorptive power A careful microscopic examination showed no evidence of fusion even on sharp edges

1 cc ultra clay (heated to 110°) adsorbed 93 0 cc NH_3
1 cc. clay soil (heated to 110°) adsorbed 27.7 cc NH_3
1 cc. clay soil (heated to 1130°) adsorbed 1 4 cc NH_3

"Deducting 1.4 cc. ammonia adsorbed by material, presumably not colloidal, from 27.7 cc. adsorbed by the unaltered soil leaves 26 3 cc. adsorbed by the colloid of the soil. Therefore, if the pure colloid adsorbs 93 0 cc ammonia and there is sufficient colloid in the soil to adsorb 26.3 cc. ammonia, the colloidal content of the soil must be 28 3 per cent."

The author's improved method of determining the colloid content of soils by adsorption of a dye (malachite green) is worth using. It is given on page 529 of the reference cited.

Exp. 160. (2) The Effect of Sodium Hydroxide on Clays.[1]—Wash a sagger clay or ball clay free from soluble salts, completing the washing in a dialyzer. It may be well to use parchment paper that has been soaked in distilled water to remove any soluble sulfates left from the sulfuric acid treatment.

Shake 50 g with enough water to give a depth of 15–20 cm. in the comparison tubes. Prepare a series of suspensions of this clay in sodium hydroxide solutions of the following concentrations 0.001 N, 0 002 N, 0.004 N, 0 008 N, 0 012 N, 0 020 N, 0 35 N, etc Prepare a similar series, using kaolin instead of this clay. After ten or fifteen minutes, marked differences in the depth of suspend solid are observed At what concentration has sodium hydroxide its maximum suspending power?

Exp. 161.—Measurement of Plasticity of Clay.—According to Bleininger, "Plasticity is sometimes measured by letting 1 g of clay stand in a solution of normal sodium carbonate, then determining the amount adsorbed by the decrease in the strength of solution. The amount of sodium carbonate adsorbed is supposed to be proportional to the colloids, which colloids are supposed to be the seat and source of plasticity" Of course, the student will use any convenient amount of clay and calculate the adsorption per gram. The sodium carbonate probably precipitates those bases which are combined with gels.

A. S. Watts finds that the most satisfactory indicator of actual plasticity is the amount of water required to render a given amount of clay sufficiently fluid so that it will not adhere as a globule to a 1 centimeter (inside diameter) nickel-plated polished loop of No. 20 wire. With this method it is easy to study the effect of alkali on clays. E. B. Matthews states that plastic clays contain particles of different size in about the proportions to give maximum density.

Exp. 162. Adsorption of Water Vapor by Soils.[2]—Place a wet sponge in the bottom of a desiccator to saturate the atmosphere with moisture. Dry a

[1]Adapted from Ashley, Technical Control of the Colloidal Matter of Clays, Bureau of Standards Bulletin No 23

[2] Adapted from Patten and Gallagher, Absorption of Vapors and Gases by Soils, Bureau of Soils Bulletin 5.

number of soils in the air and a parallel series at 100°. Use such soils as quartz sand, clay soil, loam, very heavy clay and humus. Weigh out a convenient sample (100 g. to 200 g) of each soil on a shallow dish and place in the moist atmosphere of the desiccators for twenty-four hours. Weigh again and compare the speed with which each soil takes up moisture. Since this is the reverse of drying out, it is a measure of the strength with which water is held by each soil.

From these results it may be concluded that the adsorptive capacity of soil for water vapor is generally higher the finer the texture of the soil and the greater its content of humus. It appears, too, that productive soils have a very considerable capacity for water vapor while the poor soils range much lower.

Exp. 163. The Effect of Variations in Humidity upon Soils.[1]—The effect of atmospheric humidity changes upon soils may be experimentally reproduced by placing several equal portions of a soil of known moisture content in desiccators whose individual atmospheric humidity is maintained practically constant by sulfuric acid, differing in strength for each desiccator and thus giving a range of humidity from the very low partial pressure of concentrated acid to the vapor pressure of water at the temperature chosen for the experiments.

Heat changes may be studied by running equilibrium experiments similar to those just described, but at different temperatures, and comparing the quantities of moisture in soil and in vapor above it at each temperature

One of Patten and Gallagher's experiments is graphically presented here

Exp. 164.—Test Fickendey's statement that more alkali is required to precipitate (flocculate) natural clay than kaolin on account of the protective action of humus.

For other soil experiments see the chapter on adsorption from solution, Experiments 120, 121, 122

ADDITIONAL REFERENCES

Russel, Second Report on Colloid Chemistry by the British Association, pages 70–81.

Patten and Waggaman, Bulletin 52, U S Bureau of Soils.

Cushman, Jour Am. Chem Soc , **30,** 779 (1908).

Cushman, Bulletin 104, U S Bureau of Soils

[1] Adapted from Patten and Gallagher, Bureau of Soils Bulletin No 31

CHAPTER XVI

SPECIAL TOPICS

EXPERIMENTS ON DYEING [1]

Exp. 165. Dyeing with a Direct or Substantive Dye.—After thoroughly shaking the standard direct dye solution [2] found on the reagent shelf, transfer four 40 cc. portions to beakers or flasks. Add 10 cc of water to three of the solutions. To the fourth add 10 cc. of a saturated solution of sodium chloride. To the second and third dye baths add 0 2 cc. and 1.0 cc. of the saturated NaCl, respectively. Label the solutions so that you will know the amount of salt in each, and then heat them to boiling. Place a piece of cotton or woolen cloth, 1 inch square, in each bath and allow the solutions to simmer for twenty minutes. Remove the cloth, rinse once in cold water and dry. Compare the different pieces How does the intensity of the color vary with the amount of NaCl present in the bath? The direct dyes are in colloidal solution. Can you explain your results in terms of colloid chemistry?

Reference: Pelet-Jolivet, Zeitschr. Chem. Ind. Kolloid., **5**, 235 (1909); Chemical Abstracts, **4**, 829 (1910).

The dye taken up will pass through a maximum as the amount of NaCl or other salt added is increased. The reason seems to be that the dye is destabilized by the added salt before coagulation takes place. Decreasing the peptizing or stripping action of the solvent means increased adsorption.

Exp. 166. Dyeing with an Acid Dye and the Effect of Glauber's Salt.[3]—Into each of four 250 cc. beakers or flasks measure 25 cc of the standard acid-dye solution [4] found on the reagent shelf. Then add exactly 5 0 cc. of 0 1 N hydrochloric acid [5] to two of the solutions and exactly 0.5 cc. of

[1] Contributed by Professor W. D. Bancroft, Cornell University.

[2] The direct dye standard solution should be a 0.1 per cent solution or suspension of any of the usual direct dyes Erie Red 4B Conc., Buffalo Direct Blue G Conc. and Erie Direct Green are typical examples.

[3] Contributed by Professor W. D Bancroft, Cornell University

[4] The standard dye solution may be made up from any acid dye which is present in true solution. Orange II, Lake Scarlet, Croceine Orange, Acid Green or Crystal Ponceau are typical examples. The standard should contain 1 5 grams of dye per liter

[5] It will be best to supply the laboratory with a bottle of this acid connected with a burette, so that amounts can be measured accurately. The acid need only be approximately 0 1 N.

0 1 N hydrochloric acid to each of the other two. Twenty-five cc. of 0 1 N sodium sulfate are then added to one of the solutions containing the 0.5 cc. of acid and to one of the solutions containing 5 0 cc of the acid Add water to all four dye baths until the total volume in each case is 125 cc Heat the four solutions to boiling and then add a half gram of wool yarn to each bath, making sure that the wool is thoroughly wetted by the solutions.[1] Cover the dishes with watch glasses to prevent excessive evaporation and maintain at a slow boil for thirty minutes. Remove the wool samples before the bath cools and rinse them once quickly in cold water. Dry and compare the resulting shades and also compare the intensity of the partially exhausted dye baths. Explain your results

References: Bancroft, Applied Colloid Chemistry, 115 (1921); Jour. Phys. Chem., **18,** 10 (1914). Davison, Jour. Phys. Chem , **17,** 737 (1913).

RUBBER [2]

Rubber latex is a colloidal suspension or emulsion of caoutchouc in a watery liquid with protein as the emulsifying agent. Coagulation is produced by evaporation, by smoking, or by adding certain reagents which change the physical condition of the protein films. Vulcanization by heating with sulfur is probably a colloidal process, although some chemists dispute this.

Rubber exhibits the ordinary properties of gels, often to an extraordinary degree.

NOTE —A short dissertation on rubber will be found on pages 251–262 of "The Chemistry of Colloids," by Zsigmondy and Spear (John Wiley & Sons). Simmon's book on "Rubber Manufacture" (D. Van Nostrand Co), is also useful

Exp. 167. "Tackiness," Plasticity.—Place a strip of raw rubber about 1 inch wide upon a wooden block and pound the rubber severely with a hammer. Note the rise of temperature Touch two portions of the pounded surface together. It has become sticky, or "tacky," and more plastic In this state it can be easily molded by pressure. This property is made use of in the production of most rubber goods.

We are not sure of the reasons for this extraordinary change of properties brought about by mechanical manipulation. It is ascribed to a depolymerization of the rubber, but whether this is due to a mechanical subdivision of the particles, or to a readjustment within the molecule is not known

Exp. 168. Elongation of Rubber Which Has Been "Cured" (vulcanized

[1] Instead of being weighed out, the wool can be measured by length if in the form of yarn. A heavy knitting worsted will require about 50 inches for a half gram

[2] Contributed by Ellwood B Spear, Goodyear Rubber Co

to a desirable degree).—Fasten a clamp of known weight to each end of a shoe-string strip of well-cured rubber. An elastic band will serve the purpose. Put two marks, 1 inch apart, near the center. Attach one end to a stand or beam and let the other end hang down. Attach a light scale-pan of known weight to the lower clamp Add weight to the scale-pan so that the rubber will be stretched 100, 200, 300 per cent., etc , until the strip breaks. A good piece of rubber will stretch 600 to 1000 per cent Plot the per cent stretch as ordinates and the corresponding weights as abscissæ. The line connecting the points is called the stress-strain curve. These curves are characteristic of the state of the gel Many factors enter into these considerations, for instance, the amount of combined sulfur, the kind of raw rubber used, the amount and kind of compounding materials present and the sort of accelerator employed.

Exp. 169. Swelling, Solvation.—Raw rubber will swell in a few hours if covered with turpentine, benzene, gasoline, carbon disulfide, carbon tetrachloride or any one of several other solvents It will not swell in water, amyl alcohol or acetone. Try it. Well-cured rubber, on the other hand, swells only moderately in benzene or gasoline Try it

Exp. 170. Rubber Sols.—Cut raw rubber, recently milled rubber (well-pounded rubber will do) and well-cured rubber into small pieces. Add just enough benzene to each lot in separate vessels to cover the solid, and allow to stand for several hours, preferably overnight Stir by means of a mechanical device and add benzene in small portions until the solution is 5 to 10 per cent rubber The raw and milled rubber will form colloidal solutions, while the cured rubber will be practically unaffected.

Exp. 171.—Make viscosity determinations on the sols immediately after the solutions are prepared and again after several days. The viscosity of milled-rubber solutions increases on standing

Exp. 172. Precipitation of Rubber. Reversibility of Colloid.—Add alcohol or acetone to the benzene or gasoline rubber sol in small portions. Shake well between each addition. The rubber will be precipitated as a sticky, sometimes stringy, curd. The curd may be redissolved in benzene or gasoline

Experiments on gelation, syneresis or drying may be performed with rubber sols in a manner similar to that employed in the case of gelatin Rubber sols gradually merge into doughs as the concentration of rubber is increased.

Exp. 173. Rubber as a Solvent.—Azo-benzene may be milled into rubber (50–50 mixture by weight) so that the former dissolves above 60°. When it cools distinct crystals appear and may be seen with the ordinary microscope.

Azo-benzene placed on the surface of dry, pale crepe rubber diffuses perceptibly in twenty-four hours.

To a benzene solution of azo-benzene add strips of pale crepe rubber The rubber swells to a beautiful clear gel, colored throughout. Or make a rubber-benzene gel and drop crystals of azo-benzene on top In half an hour it will have uniformly diffused throughout the gel.

If such a gel, containing equal weights of azo-benzene and rubber, is allowed to stand in an open vessel, the benzol evaporates and, after some hours, crystals of azo-benzene appear on the surface

Exp. 174.—Rubber as an Emulsifying Agent.—Shake various liquids with any convenient rubber solution (such as 2 per cent rubber in benzene) If emulsions are formed let them stand, and note time of creaming and time of breaking. Is the benzene the continuous or the dispersed phase? Why?

"HOPCALITE"

CATALYSIS OF THE REACTION BETWEEN CARBON MONOXIDE AND OXYGEN

Exp. 175.—"Hopcalite," as developed during the Great War by J. C. W. Frazer, A. B. Lamb and W. C. Bray, for gas masks, was a mixture of MnO_2, 50 per cent; CuO, 30 per cent, Co_2O_3, 15 per cent; and Ag_2O, 5 per cent. The process of manufacture involved the separate precipitation and washing of the manganese dioxide, copper oxide and cobaltic oxide and the subsequent precipitation of the silver oxide in the mixed sludge After further washing, the sludge was filtered, kneaded, dried and ground to such sizes that 52 per cent passed through an 8–12 mesh screen, although not more than 6 per cent passed a 14–16 mesh screen.

The catalytic activity of the mixture depends in large measure on the method of preparation of the manganese dioxide The first really active manganese dioxide was made by reducing a cold solution of ammonium permanganate with methyl alcohol. A large-scale process used depended on the reaction between potassium permanganate and anhydrous manganese sulfate in the presence of fairly concentrated sulfuric acid. When prepared by oxidation of a manganous salt in neutral or alkaline solution, the manganese dioxide was not catalytic (or, rather, Hopcalite containing it was not).

Fremy's method (Compt. rend, **82**, 1231, 1876) furnished the best manganese dioxide. To 150 g. of potassium permanganate was added a cooled mixture of 500 g. of concentrated sulfuric acid with 150 g. of water, and the mixture was allowed to stand several days, during which time the permanganic acid was slowly decomposed with evolution of oxygen. The mixture was then poured into a large volume of water and the resulting finely divided manganese dioxide washed, first by decantation and then on a filter, until the filtrate showed no test for sulfate The precipitated oxides of manganese, copper and cobalt, were suspended uniformly in water and added, with stirring, to a silver nitrate solution containing sufficient silver nitrate to give the desired amount of silver oxide Sodium hydroxide solution was then added, with vigorous stirring, until a distinct alkaline reaction was observed. After thorough washing the mixture may be collected as a filter cake on a Buchner funnel The material was dried on a water bath, broken up, then slowly heated to 120°–130°, meshed, and finally dried for a short time at 200°

Prolonged heat treatment at a high temperature spoils these catalysts, presumably on account of the destruction of the porous nature of the granules.

Water vapor poisons this catalyst; therefore the mixture must be heated a few hours to about 150° before use, to activate it In the gas masks, the air was dried by granular calcium chloride before coming in contact with the Hopcalite

Exp. 176.—Pass a stream of air, dried over anhydrous calcium chloride, through a pyrex tube (1 cm. diameter) containing a 2–3 cm layer of Hopcalite. The catalyst may be held in place by means of copper gauze plugs. Water gas (because of its carbon monoxide content), or even prepared carbon monoxide, may be introduced into the air stream, and as the concentration of the

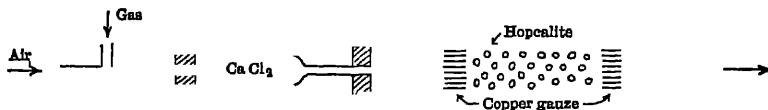



Fig. 31.—Catalysis with Hopcalite

carbon monoxide is increased the contact layer becomes warm If the concentration is sufficiently high the contact material will reach a red heat. Test the issuing gas for carbon dioxide.

The author is indebted to A. T. Larson, of the Fixed Nitrogen Research Laboratory, for suggestions on this experiment. Much material was taken directly from the paper by Lamb, Bray and Frazer in Jour. Chem. Ind. Eng., **12**, 213, 1920.

CATALYTIC REDUCTION

We quote from page 192 of " Catalysis in Theory and Practice," by Rideal and Taylor, The Macmillan Co.

" The theoretical investigations of Paal and his co-workers, of Willstatter and others have demonstrated conclusively that numerous hydrogenations can be effected in presence of finely divided platinum or of colloidal palladium as catalyst. In general, it was found necessary to stabilize the colloidal metal, and various protective colloids were employed to effect this.

Skita, who in his book " Über Katalytische Reduktionen Organischer Verbindungen " (F. Enke, Stuttgart, 1912) has detailed in a comprehensive manner the literature of the subject, employed an acid—stable protective colloid such as gum arabic in place of the agents used by Paal. Solutions of platinum or palladium chloride in presence of such protective agents are reduced to stable colloidal solutions of the metal by means of hydrogen in the cold. The protective colloid also has the power of preventing the precipitation of the hydroxide of the metal when sodium carbonate is added to the solutions, the metal remaining in colloidal suspension Such colloidal suspensions have proved to be excellent hydrogen carriers for hydrogenation of both aromatic and aliphatic unsaturated compounds."

Lochte, Bailey and W. A. Noyes, Jour. Am. Chem. Soc. (**43,** 2597, 1921) used colloidal platinum in reduction.

"The Skita apparatus (Ber. **45,** 3578 and 3589, 1912) is used, the container for the reduction mixture being a 1 ter flask. This bottle is charged with 25 g. of hydrazine hydrate in 100 cc. of water. To this is added a mixture of 0.5 g. of gum arabic dissolved in 50 cc. of water and 10 cc. of chloroplatinic acid. The 'seeding' colloid is next prepared by mixing 10 cc. of water, a few drops of gum arabic solution, 5 cc. of chloroplatinic acid, 0.5 cc. of 30 per cent sodium hydroxide, and a few crystals of the hydrochloride of symmetrical di-isopropyl-hydrazine, or some equally good reducing agent. On heating this mixture reduction of the platinum begins at once. The hot mixture is rapidly added to the solution in the flask, to which are then added, under thorough shaking of the flask, 100 cc. of 18.5 per cent hydrochloric acid and finally 100 cc. of acetone. The flask is then connected to the apparatus, the system evacuated and filled with hydrogen from a cylinder, until the apparatus is under a total pressure of two atmospheres. The hydrogen cylinder should be supplied with a reducing valve to prevent accidents and damage to the apparatus in filling the reservoir and flask.

"The room temperature, hydrogen pressure, atmospheric pressure and gage readings are now recorded and the shaker started. During the few minutes required for the reduction of the chloroplatinic acid the absorption is relatively slow, but as reduction of the platinum proceeds the rate of absorption increases until the gas is used up at the rate of 8 to 12 liters an hour. As reduction proceeds the absorption of hydrogen gradually slows down and comes to a complete stop at the end of 3 to 4 hours, when the theoretical amount of hydrogen has been absorbed. In case of poisoning of catalyst or other causes of slow reduction an additional 5 cc. of chloroplatinic acid is sometimes required to complete the reduction."

In the above experiment the purpose was to reduce hydrozine hydrate to symmetrical di-isopropyl-hydrazine.

T B. Johnson and E B Brown will soon publish a description of their practical apparatus for reduction of large quantities of reagents on a quantitative basis. They do not use any promoter other than hydrogen to prepare their colloidal platinum.

LUBRICATION

J. E. Southcombe examined the causes of the superior lubricating efficiency of fatty oils over mineral oils. Using a Donnan pipette, he compared the drop numbers of various oils in water as a measure of surface tension of oil against water.

The number of drops for a given volume of oil was 101 for a pure mineral oil, 148 for a cocoanut oil containing 4 per cent free fatty acid, 130 for a mineral oil containing 3 per cent fatty acid, and 108 for rape oil with 0.15 per cent acids. This shows the lower surface tension of fatty oils as well as the marked lowering of surface tension caused by dissolved fatty acids.

Repeat Southcombe's experiment. See if there is any difference between saturated and unsaturated fatty acids (stearic and oleic) or between the acids of low and those of high molecular weight

The "germ theory" of lubrication is based upon such experiments. Usually about 2 per cent of free fatty acids, made from rape oil, is added to a mineral lubricating oil with good results.

Exp. 177. Mechanism of Lubrication.—The effect of adsorbing the film of oil on a surface may be shown by placing a highly polished block of metal which has been oiled, on the wooden surface of an inclined plane, gradually raising the inclined plane by means of a vertical screw arrangement, until the metal just starts to slip, noting height of plane and obtaining coefficient of friction. Repeat above experiments, using some oils to which unsaturated compounds, such as oleic acid, have been added

A method for comparing the oiliness of lubricants was invented by Deeley (Proc. Phys. Soc., London, **32**, Pt. II, 1–11, 1920). He used a machine having three pegs resting on a flat disk of metal which could be slowly rotated. The pegs were attached to an upper dish which, in turn, was attached to a spiral spring and index finger.

W. B. Hardy and H. K Hardy are well quoted in Chemical Abstracts, **13**, 2805 (1919) on theories of lubrication. Try their experiments with the slipping watch glass. W. B. Hardy in Jour. Soc. Chem. Ind., **38**, 7t (1919) assures us that we may look with confidence to colloid chemistry to aid us in finding the lubricants of the future.

It is stated by Stanton, Archbutt and Southcombe (Eng., **108**, 758, 1919) that when the pressure is raised to about 900

atmospheres the viscosity of vegetable and animal oils increases fourfold while that of mineral oils increases sixteenfold. Hence, viscosity is not the most important factor in difficult lubrication. "Oiliness" is attributed to adhesion or chemical affinity between the metal and the lubricant. The addition of 1 per cent free fatty acids of rape oil to a certain mineral oil lowered the friction coefficient from 0.0047 to 0.0033, equal to the benefit from the addition of 60 per cent neutral rape oil.

An excellent abstract of a "Discussion on Lubrication held at the Imperial College of Science and Technology" was written by Bingham for Chemical Abstracts, **14**, 1475 (1920).

FLOTATION

Read Jour. Ind Eng. Chem, May (1917); Jour. Phys. Chem, **19**, 275 (1915); any volume of Trans Am. Inst. M E; "Flotation," by Rickard and Ralston; "Flotation," by McGraw; "Flotation," by Taggart.

Exp. 178.—Clean a needle in soda solution (handling with pincers). Dry on a clean cloth. Lay on a floating tissue paper. Depress the paper gently with a stick. The paper sinks and the needle floats on the "surface skin" of the water If greased, a larger needle can be floated. A glass rod of the same diameter, but lighter, sinks because it is easily "wetted" by water while the steel needle is not Grease the glass rod and it floats. Glass and steel typify the gangue and sulfide of flotation ores.

Exp. 179.—By addition of enough oil, surface tension is lowered from 73 to 14 dynes per linear centimeter Lay a match on the surface of water, then a drop of olive oil near the match The match draws away because the oil has reduced the tension of part of the water surface, and therefore the purer water on the other side pulls away.

Exp. 180.—Drop oil on wet galena Oil displaces the water Drop oil on wet quartz. There is no displacement.

Drop water on oiled quartz Water displaces the oil Which liquid "wets" quartz? Which wets galena?

Exp. 181.—Grind quartz and a sulfide ore (CuS or ZnS) to pass a 48-mesh sieve. Flotation ores are usually ground wet in practice Pour into a separatory funnel, add more water and shake There is no froth Now add a drop or so of creosote oil Violent shaking should produce a good froth, carrying the sulfide. Run out the liquid and sludge, put the froth on a hot plate to dry, and examine with the microscope or analytically to see if the "floated" material is richer than the ore

A simple laboratory experiment with hand shaking of flasks is described by W. H. Coghill in Chem Met Eng **20**, 537, 1919.

It may be seen from the above experiments that sulfides (and other minerals of metallic luster) may be separated cheaply from

the waste rock (gangue) in which they occur. Preferential wetting of the sulfide by the oily froth balloons the heavy sulfide particles to the floating froth while preferential wetting of the gangue by water carries gangue particles to the bottom. The froth is then skimmed off and broken. Air is beaten into the wet pulp of ground ore and water to which a very little pine oil or other oil has been added to secure a froth. Over 60,000,000 tons of ore are " floated " in this way every year and the recovery is much higher than by older methods.

Exp. 182. " Colloidal Garden."—Dilute ordinary commercial water-glass syrup with a nearly equal volume of water and put into a tall, wide-mouthed bottle Drop in solid fragments (about half the size of a pea) of ferric chloride and cobalt chloride (be sure to use these two), as well as salts of nickel, copper and manganese As the solids dissolve, the solution reacts with sodium silicate to form gelatinous membranes of copper silicate, etc The little sack is, of course, filled with a very concentrated solution of copper salt of higher osmotic pressure than the solution outside. Naturally, water enters the sack faster than it leaves, and bursts the sack (upwards because there is less hydrostatic pressure at greater heights) New membrane forms, and the final growth is tree-like in appearance Ferric chloride trees grow rapidly, a matter of inches in a few minutes, and cobalt chloride trees make noticeable growth The others are much slower

Exp. 183. Carrying of Mercury on Iron Gauze (No. 40 of Bancroft's Colloid Problems).—Lord Rayleigh (Scientific Papers, **4**, 430, 1903) pressed a piece of iron gauze down on the flat bottom of a glass vessel holding a shallow layer of mercury, and found that the gauze remained on the bottom of the vessel and did not rise through the mercury The reason for this is that the mercury does not wet the iron A corollary from this, which has not been tested experimentally, is that one should be able to carry mercury in an iron sieve just as one can carry water in an oiled sieve (Chwolson, Traité de Physique, **1**, III, 613, 1907) Since sodium amalgam wets iron, a dilute sodium amalgam should run through an iron sieve which would stop pure mercury. Also, Rayleigh's experiment would not succeed if a sodium amalgam were substituted for the mercury.

ULTRAFILTRATION

Read Bechhold, 95–102; Zsigmondy, 38–39; Alexander, 26–28; Hatschek's Laboratory Manual, 69–76; Schoep, Kolloid-Zeitschrift, **8**, 80 (1911). Schoep used collodion to which castor oil and glycerin had been added. Paper thimbles were soaked in this. They became more permeable as the content of glycerin and oil increased. No extra pressures were needed.

Exp. 184.—A simple ultrafilter may be prepared by pouring a 4 per cent collodion solution on a wet filter paper, folded in the funnel. Tilt to secure a uniform coating, pour out the excess, add a fresh solution, and repeat A film of cellulose nitrate is precipitated in such form that it serves for some colloid separations. Schoep's device of tying a collodion sack to the flanged end of a funnel, so that it hangs inside a filter flask, is useful. This introduces some pressure.

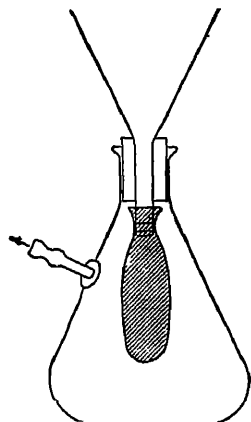



FIG 32 —Schoep's ultrafilter

IMBIBITION OF GELATIN[1]

Exp. 185.—Cut thin sheets of the purest commercial gelatin (such as Coignet's) into pieces about 1 inch square Determine the moisture and ash contents of the gelatin and assume the rest to be dry gelatin. Weigh exactly the equivalent of 1 g. dry gelatin into each of 12 wide-mouthed 6-oz. bottles and add 100 cc. of HCl, using a different strength for each, use the following normalities: 0 005, 0 010, 0 015, 0.020, 0 030, 0 050, 0 075, 0 10, 0 15, 0 20, 0 25 and 0.30. Let stand for forty-eight hours and keep at a temperature not exceeding 18°, preferably at constant temperature Then carefully remove the gelatin plates from the solutions, by means of a wide spatula, blot off adhering moisture with filter paper, pile on to a watch glass, and weigh Then put the gelatin plates, as quickly as possible, into clean, dry bottles, add more dry NaCl than will dissolve, and let stand for another forty-eight hours

In the meantime, calculate, from the increase in weight of the gelatin plates, V, the number of cc. of acid solution which the gelatin has absorbed Titrate aliquots of the remaining acid solutions to obtain x, the concentration of HCl in the external solution Plot V against x and note the peculiar nature of the curve. Why is this preferable to plotting V against the initial concentration of acid, as is sometimes done?

From $(100-V)x$, the milligram-equivalents of acid not absorbed, and the quantity of acid used initially, calculate a, the quantity absorbed Plot a against the initial concentration of acid and compare with any so-called adsorption curves.

At the end of the second forty-eight-hour period, remove the gelatin plates from the saturated salt solutions, and weigh Calculate the volume of salt solution in the gelatin Titrate the salt solutions in the bottles, using methyl orange as indicator, and record as b the quantity of acid removed from the gelatin by salt Assume (not strictly true) that the salt solution remaining in the gelatin has the same concentration of acid as that titrated, and calculate c, the quantity of free acid still left in the gelatin If the quantity $(b+c)$ represents the free acid in the absorbed solution before adding salt, its concentration was $(b+c)/V$, or y What relation does y bear to x? Subtract

[1] Contributed by John Arthur Wilson, of Gallun & Co , Milwaukee.

$(b+c)$ from a to get d, the quantity of acid removed from solution. Plot d against x and compare with the curve for a. Does it suggest anything regarding the nature of the removal of acid by gelatin? Does it enable you to calculate the combining weight of gelatin?

If time permits, repeat the experiment, using sulfuric acid and sodium sulfate. Get swelling curves also for acetic acid, lactic acid, and boric acid.

NOTE.—It will be noted that Dr. Wilson's views on swelling and adsorption are not exactly the same as those expressed by some other writers quoted in this manual.

After performing these experiments, study:

1. The Action of Dilute Acids and Salt Solutions on Gelatin, by H. R. Procter, Koll.-Chem. Beihefte, p. 243, 1911, or Jour. Am. Leather Chem. Assn., p. 270, 1911.

2. Colloidal Phenomena and the Adsorption Formula, by J. A. and W. H. Wilson, Jour. Am. Chem. Soc., p 886, 1918.

3. Imbibition of Gels, by J. A. Wilson, Third Report on Colloid Chemistry, 1920 (British Assn. for the Advancement of Science).

CHROME TANNING[1]

Exp. 186.—Pass sulfur dioxide gas through a strong solution of sodium dichromate until all dichromate has been reduced This is now a commercial "chrome liquor" From this stock liquor make up 10 solutions of 200 cc. each, of different concentrations. Use the following strengths given in terms of grams Cr_2O_3 per liter 0 2, 0 4, 1 0, 5 0, 10.0, 15.0, 20 0, 50 0, 100.0 and 200.0. Into each bottle put 5 g of Standard hide powder (Standard Mfg Co., Ridgway, Pa). Shake at intervals for forty-eight hours and then filter. Analyze each filtrate for chromic oxide. Assume that the decrease in concentration of the chrome liquor is a measure of the amount of chromic oxide adsorbed by hide substance, and plot the calculated amount adsorbed against the initial concentration of the liquor. How can you explain the negative values for the higher concentrations? What false assumption was involved in the calculation? Now wash the tanned powders free from soluble matter, dry them and analyze for chromic oxide and hide substance (nitrogen $\times$ 5 62). Plot the value for grams chromic oxide fixed by 1 g hide substance against the concentration of the liquor after tanning Does chrome tanning follow the so-called adsorption formula?

Read "The Effect of Concentration of Chrome Liquor upon the Adsorption of its Constituents by Hide Substance," by A. W. Thomas and M. W. Kelly, Jour. Ind Eng. Chem., **13**, 65, 1921.

[1] Contributed by John Arthur Wilson, of Gallun & Co , Milwaukee

Osmotic Pressure of Colloids.—For a very complete discussion of osmotic pressure of colloids, read Ostwald's "Handbook of Colloid Chemistry," 231–262; also Zsigmondy's "Chemistry of Colloids," 38.

Glues.—The Technical Notes of the Forest Products Laboratory at Madison, Wis., give a vast amount of valuable information on glues and glue testing.

A useful paper on glues by R. H. Bogue is found in Chemical Age, **30,** 103, 1922.

Pure Fibrin.—For the preparation of pure fibrin, read a paper by A. W. Bosworth (Jour. Biol. Chem. **20**, 91, 1915).

Pure Casein.—Van Slyke and Baker, Jour. Biol. Chem., **35,** 127 (1918), give an excellent method for the preparation of pure casein.

Photometric Methods.—Sheppard and Elliott, Jour. Am. Chem. Soc., **43,** 531 (1921), outline some useful photometric methods and apparatus for the study of colloids.

In Chem. Met. Eng., **23,** 1005 (1920) Alsberg presents some suggestive colloid problems.

BRIEF BIBLIOGRAPHY

1. Jerome Alexander: "Colloid Chemistry." 90 pp. D. Van Nostrand Co., New York City, 1919. Deals largely with the practical applications of the science.

2. Plimmer: "Practical Organic and Bio-Chemistry," Longmans, Green & Co., New York, 1918. In pages 374–391 is given a clearly-written introduction to colloid chemistry.

3. Emil Hatschek: "An Introduction to the Physics and Chemistry of Colloids." 172 pp P. Blakiston's Son & Co., Philadelphia, 1922. Based on a course of ten lectures. A useful introduction to colloids Third edition.

4 Wolfgang Ostwald. "Theoretical and Applied Colloid Chemistry" Translated by Martin Fischer. 232 pp John Wiley & Sons, Inc., New York City, 1917. Revision of a course of five lectures given in the United States a few years ago. A very stimulating book. Second edition in press

5. Zsigmondy: "The Chemistry of Colloids." Translated by Spear. 288 pp John Wiley & Sons, Inc., New York City, 1917. One of the most useful books of its size on the subject yet published. Contains 33 pp. on the industrial applications of colloids.

6 W. D. Bancroft: "Applied Colloid Chemistry." 345 pp. McGraw-Hill Book Co., Inc, 1921. Written at the request of the Committee on the Chemistry of Colloids A stimulating book, full of illuminating comments on the work recorded in the literature. Especially strong in treatment of adsorption Every colloid chemist should own this book.

7 Freundlich: "Kapillarchemie." 591 pp. Leipzig. 1909. The greatest classic in the literature of colloids.

8. Wolfgang Ostwald. "Handbook of Colloid Chemistry." Translated by Martin Fischer. 284 pp. P. Blakiston's Son & Co., Philadelphia, 1919 Gives valuable references to the literature A translation of Ostwald's "Grundriss der Kolloidchemie" Second edition

9. Bechhold: "Colloids in Biology and Medicine." Translated by Bullowa from second German edition 464 pp. D. Van Nostrand Co., New York City, 1919. A useful book, somewhat specialized as the title indicates, but valuable to any student of colloids. Contains 40 pp. on "Methods of Colloidal Research," including much of the author's own work on ultrafiltration.

10 Taylor: "Colloids" 327 pp. Longmans, Green & Co, New York City. Not very well arranged Contains some useful directions for the preparation of colloids Should be used only as a reference book on isolated points

11 Burton: "Physical Properties of Colloid Solutions." 197 pp. Longmans, Green & Co., New York City, 1916. Contains a good bibliography. Rather physical in treatment.

12. The Svedberg: "Herstellung Kolloider Lösungen." 507 pp. Theodor Steinkopf, Dresden, 1909. A classic Gives full directions for preparing hundreds of colloids. Contains a valuable bibliography.

13. Trivelli and Sheppard "The Silver Bromide Grain of Photographic Emulsions." 143 pages. D. Van Nostrand Co, New York City. A splendid monograph, the first of a series.

14. Martin Fischer: "Œdema and Nephritis." 3d ed. 922 pp John Wiley & Sons, Inc, New York City, 1920. Outlines and defends a treatment of disease based on the principles of colloid chemistry.

15. First, Second and Third Reports on Colloid Chemistry and Its General and Industrial Applications, by the British Association for the Advancement of Science. At H M Stationery Office, 128 Abingdon St, London, S W. 1. Each report (about 160 pp) contains chapters on special fields by eminent authorities. Thorough reviews, numerous references An invaluable colloid library Each report costs 2/6d

16 The Physics and Chemistry of Colloids (report of a general discussion held by the Faraday Society and the Physical Society of London, Oct. 1920) Gels are discussed at length. Published by His Majesty's Stationery Office, London.

17. Martin Fischer "Soaps and Proteins." 272 pp. John Wiley & Sons, New York City, 1921. A study of soaps as solvated colloids Their similarity to proteins in many respects is pointed out for the benefit of the physician. Yet the commercial side of soap manufacture is not neglected A brilliant production.

18. Martin Fischer and Marian Hooker: "Fats and Fatty Degeneration" 146 pp. John Wiley & Sons, Inc., New York City, 1917. Theories of emulsification discussed, especially in relation to body tissues.

19 U. S Bureau of Soils, Bulletin **52**, "Absorption by Soils." 95 pp. 1908. Very useful.

20. U. S Bureau of Soils, Bulletin **51**; "Absorption of Vapors and Gases by Soils." 1908.

21. Ashley "Technical Control of the Colloidal Matter of Clays." U S Bureau of Standards, Technologic Paper **23**. 115 pp Written in 1911.

22. Bancroft· "Applied Colloid Chemistry" Chem. Met. Eng, **23**, 454 (1920). A brief survey of the field.

23. W. C McC Lewis· "Some Technical Applications of Capillary and Electrocapillary Chemistry," Met. Chem Eng, **15**, 253–259 (1916); also Jour. Soc. Chem Ind., May 31, 1916 Somewhat like the book by Alexander (No. 2).

24. Whitney and Ober: Jour Am. Chem. Soc, **23**, 856–863 (1901). Gives an excellent bibliography, with brief comment, of colloid work published before 1901 Nearly 150 references

25. A. Müller "Bibliography of Colloid Chemistry," Zeit. anorg Chemie, **39**, 121 (1904). Three hundred and fifty-six references grouped by subjects, without comment

26 Höber: "Physikalische Chemie der Zelle und Gewebe" Wilhelm Engelmann, Leipzig, 1911

27 Rideal and Taylor: "Catalysis in Theory and Practice" The

Macmillan Co., New York, 1919 Not primarily a colloid book but contains material of value to colloid chemists. A new edition is promised.

28. Bancroft: "Research Problems in Colloid Chemistry," No 13. Reprint issued by the National Research Council. Originally published in the Jour Ind. Eng Chem , **13,** 83, 153, 260 and 346 (1921) A list of 200 colloid problems so well presented that the reader inevitably thinks of several more Invaluable.

29. Alexander: "Some Practical Applications of Colloid Chemistry," Jour Ind. Eng. Chem , **12,** 434 (1920).

30 Bleininger. "Ceramic Processes Associated with Colloid Phenomena," Jour Ind. Eng Chem., **12,** 436 (1920).

31 Sven Oden "Der Kolloide Schwefel" Upsala, 1913. An exhaustive study of the colloidal forms of sulfur. J J van Bemmelen's "Die Absorption," 1911, is a classic of a more general nature

32 Zsigmondy: "Colloids and the Ultramicroscope." English translation of "Zur Erkentniss der Kolloide" (Jerome Alexander) Gives long quotations from the original papers of Graham

33. Svedberg: "The Formation of Colloids," 127 pp. J. & A Churchill, London, 1921. The first of a series of monographs to be written by Svedberg

34. Bingham: "Fluidity and Plasticity," 440 pp. *McGraw-Hill Co.*, New York City, 1922. A splendid work, presenting new views of some fundamental properties of colloids.

The Kolloid-Zeitschrift and Kolloidchemische Beihefte are two journals devoted to colloid research. Very important.

The Journal of Physical Chemistry contains a vast amount of invaluable material, and no student of colloid chemistry can afford to neglect this journal. Many of the articles contain exceptionally full summaries of the work done in special fields, and are really monographs. The results of colloid research, however, are found in most of the great journals.

Since many chemists waste time and become discouraged by reading the wrong book first, we urge any one of the first four in the above list as the proper introduction to the subject. These may be followed by 6, 15, 22 and the books on special topics.

Most books and articles on colloid-chemicals subjects are reviewed, abstracted or noted in the Kolloid Zeitschrift

The various journals dealing with biological chemistry frequently contain excellent colloid material.

The Decennial Index, and current indices, of the Chemical Abstracts are indispensable. The reader should look for such topics as: colloid, colloidal, glue, gel, gelatin, gum, albumin, adsorption, peptization, hydrosol, hydrogel, sol, gel, jelly, emulsion, coagulation, etc.

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